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## The Latest Development on Membrane Materials and Processes for Post-combustion CO<sub>2</sub> Capture: A Review

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### Abstract

Gas separation membranes for CO<sub>2</sub> capture becomes steadily more attractive due to its high energy efficiency, relatively low cost and low environmental impact. Different types of membrane materials such as common polymers, fixed-site-carrier (FSC) nanocomposite, microporous organic polymers and mixed matrix membranes have been developed in the last decade. This work provided the latest review on these materials and processes for post-combustion carbon capture in power plant and process industry. The membrane performance with CO<sub>2</sub> permeance >2000 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity >50 showed the potential application compared to the state-of-the-art amine absorption technology. The polyvinyl amine (PVAm) based FSC membrane, PolyActive™ and Polaris™ membranes have been demonstrated on the pilot scale for CO<sub>2</sub> capture from flue gas, and all three membranes showed quite stable performance over long-term. The gas separation membranes can be brought into commercialization in the near future by the joint force from membrane scientists and engineers.

**Keywords:** CO<sub>2</sub> capture; Membrane process; Post-combustion; Flue gas; Pilot demonstration

### Introduction

Control anthropogenic emissions of greenhouse gases (GHG), especially CO<sub>2</sub>, is one of the most challenging environmental issues related to global climate change. CO<sub>2</sub> capture and storage (CCS) is considered as the most promising way to combat global warming by reducing CO<sub>2</sub> emission to the atmosphere. The main application of CCS is likely to be at large CO<sub>2</sub> point sources: fossil fuel power plants and industrial plants (particularly the manufacture of iron, steel, refinery, cement and chemicals, and natural gas/biogas plants). Among them, fossilfuel power plants are responsible for the largest CO<sub>2</sub> emissions of 78%, followed by cement factory (7%), refinery (6%), and iron/steel plant 4.8% as shown in Figure 1 [1], and post-combustion power plants being the main contributor which need to be firstly tackled. Moreover, CO<sub>2</sub> capture from the exhaust gases in process industries, such as cement factory, refinery, iron and steel production plants should also receive attention due to its large CO<sub>2</sub> amount.

Different technologies such as chemical absorption (e.g., monoethanolamine (MEA), methyldiethanolamine (MDEA)), physical absorption (e.g., Selexol, Rectisol), physical adsorption (e.g., molecular sieves, metal organic frameworks), cryogenic distillation and membrane separation have the potential to be used for CO<sub>2</sub> capture from flue gas in power plant and off-gas from industry [2-5]. Chemical absorption is the state-of-the-art technology for post-combustion CO<sub>2</sub> capture. Some large scale CO<sub>2</sub> capture plants have been built up around the world to demonstrate the process feasibility of CO<sub>2</sub> capture from flue gas[6], and these contributions can promote the amine-based CO<sub>2</sub> capture system to be commercialized in the near future.

However, conventional amine absorption technology still faces the challenges of energy intensive and solvent degradation and emissions, which may lead to a large incremental cost and a high environmental impact. Some emerging separation technologies based on the novel absorbents of ionic liquids (high CO<sub>2</sub> solubility) and solid sorbents of microporous materials (solid adsorbents) such as zeolite, metal organic frameworks (MOFs) and metal oxides (chemical looping cycle) have been recently investigated for CO<sub>2</sub> capture. Those 3<sup>rd</sup> generation materials showed a good potential and cost reduction benefit, but most of them are in the early research phase. For more detail and in-depth understanding of absorption and adsorption materials for CO<sub>2</sub> capture, the reader can refer to the previous reviews [2-5,7-9].

Membrane separation has already been considered as an alternative and competitive technology

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**Table 1:** Representative fixed-site-carrier membranes for gas separation.

Material	Support	Membrane module	Gas separation	Reference
Poly(amidoamine)/Poly(vinyl alcohol)	-	Flat sheet	CO <sub>2</sub> /H <sub>2</sub>	[92]
Polyallylamine (PAAm) / poly (vinyl alcohol) (PVA) blend	Polysulfone	Flat sheet	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub> /CO	[93]
PVAm & PVAm/PVA blend	Polysulfone, polyphenylene oxide (PPO)	Flat sheet, Hollow fiber	CO <sub>2</sub> /N <sub>2</sub> , CO <sub>2</sub> /CH <sub>4</sub>	[53, 58, 94-98]
PVA	-	Flat sheet	CO <sub>2</sub> /H <sub>2</sub> /N <sub>2</sub>	[14]
CNT-reinforced PVAm/PVA blend	Polysulfone	Flat sheet	CO <sub>2</sub> /CH <sub>4</sub>	[99-101]
High temperature ionic liquids	Nylon	Flat sheet	CO <sub>2</sub> /H <sub>2</sub>	[102]
Room temperature ionic liquids (RTILs)	PVDF	Flat sheet	CO <sub>2</sub> /air, SO <sub>2</sub> /air, CO <sub>2</sub> /N <sub>2</sub> /H <sub>2</sub>	[103, 104]

for selected gas separation processes such as air separation and natural gas sweetening during the last two or three decades. Strong interest was put on CO<sub>2</sub> capture using gas separation membranes in the last decade, examples can be found in the literature [10-18]. However, there are still some challenges related to the membranes for post-combustion CO<sub>2</sub> capture, e.g., the limitation of membrane separation performance (the trade-off of permeance and selectivity existed in most polymeric membranes), membrane stability and lifetime. Thus, high performance membranes with relatively low production cost should be developed. Moreover, the membranes should also possess long-term stability by exposed to the acid gases of SO<sub>2</sub>, NO<sub>x</sub> and water as well as some other impurities. In 2006, the large EU project Nano GLOWA launched to develop a high performance fixed-site-carrier (FSC) membrane (developed by membrane research group at Norwegian University of Science and Technology, NTNU) for CO<sub>2</sub> capture from flue gas in power plants. A small pilot-scale membrane system was tested at Sines coal-fired power plant in Portugal over 8 months in 2011 [19]. Later on, a pilot hollow fiber FSC membrane system (membrane area 20m<sup>2</sup>) was built up and tested at Norcem cement factory where the CO<sub>2</sub> feed concentration is ca. 17 mol.% (wet-base) since 2015 at Brevik, Norway [20]. Moreover, MTR (Membrane Technology & Research, Inc.) built up a pilot-scale membrane system for post-combustion carbon capture in a 1MW coal-fired power plant using the high permeable Polaris™ membranes [21]. The PolyActive™ membranes from Helmholtz-Zentrum Geesthacht was also tested for CO<sub>2</sub> capture from real flue gas in the pilot scale [22]. Those efforts can significantly contribute to bring gas separation membrane technology into the commercial CO<sub>2</sub> capture application in the near future. In this work, a review on the recent progress of membrane materials and process development related to post-combustion CO<sub>2</sub> capture from power plants and industries was conducted.

## Membrane Materials for CO<sub>2</sub> Separation

Various types of membranes such as common polymer membranes, microporous organic polymers (MOPs), fixed-site-carrier (FSC) membranes, mixed matrix membranes (MMMs) can be used for CO<sub>2</sub> capture [4]. Different membrane materials possess various separation properties, thermal and chemical stability, mechanical strength as well as production cost, and presents their own suitable applications. Most of polymeric membranes based on solution-diffusion transport mechanism suffer the trade-off of gas permeability and selectivity, and the relatively low stability or short lifetime when exposed to acid gases (e.g., SO<sub>2</sub> and NO<sub>x</sub>). The FSC membranes presented quite good membrane performance, but how to maintain the high water vapor content in the gas stream is the challenge in engineering design. MMMs are the important research fields for CO<sub>2</sub> capture using membranes. Ghalei et al. reported a mixed

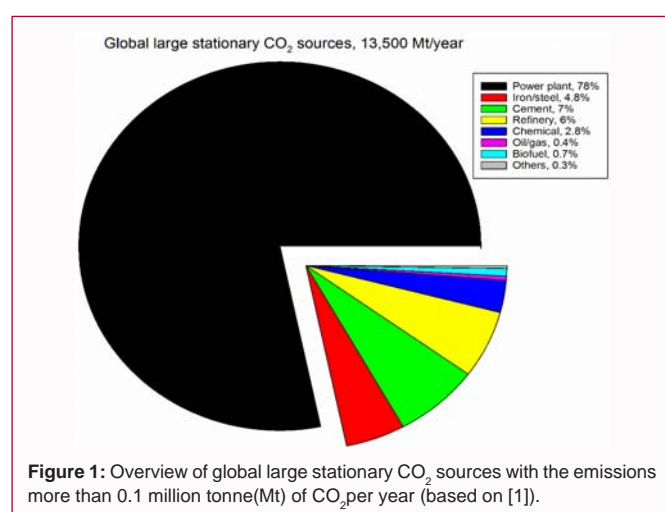
matrix membrane made from polymers of intrinsic microporosity (PIMs) incorporated with highly dispersed amine-functionalized, nanosized metal organic frameworks showed high separation performance for CO<sub>2</sub>/N<sub>2</sub> separation [23]. However, the compatibility between the polymer and the filler, and scaling-up are the main challenges in this regard. Choosing a suitable membrane material for a specific application mainly depends on membrane material properties, feed gas composition/impurities, process operating conditions as well the separation requirements. Recently, membrane separation performance has been significantly improved owing to the great effort that has been put in the membrane community. Even though most membrane materials are still in the fundamental research and will take long time to bring into commercial application, or may not be successful in the end, there are some membranes that are quite promising for CO<sub>2</sub> capture from flue gas due to the high performance and the good stability. Among them, the FSC membranes developed by the Membrane Research Group (Memfo) at Norwegian University of Science and Technology (NTNU), the Poly Active™ membranes from Helmholtz-Zentrum Geesthacht, and the Polaris membrane developed by Membrane Technology and Research, Inc. (MTR) are the frontiers in post-combustion CO<sub>2</sub> capture using membrane technology.

## Common polymer membranes

Gas permeability and selectivity are the two key parameters to characterize separation performance of a dense polymer membrane, and high performance is required to achieve separation requirements at a lower cost. However, there is a trade-off between permeability and selectivity in common polymer membranes called Robeson upper bound [24]. Gas permeability is mainly dependent on a thermodynamic factor (solubility (*S*) of penetrant in a membrane) and a kinetic factor (diffusivity (*D*)) of the gas species transport through a membrane [25]. Many researchers have used the more polar nature of CO<sub>2</sub> molecule to increase its solubility and therefore, its permeability as the size difference between CO<sub>2</sub> and N<sub>2</sub> molecules are quite small to get sufficient high diffusivity selectivity [26]. The poly(ethylene oxide) (PEO) based block copolymer materials (e.g., Pebax®) are highly-developed membranes for CO<sub>2</sub> capture. [27-29]. Highly ordered block segments was developed by University of Twente [30], they reported a high CO<sub>2</sub> permeability of 530 Barrer in the PEBAX®1657/PDMS-PEG blend membranes. The Polaris™ membrane which is a thin-film composite (TFC) structure based on Pebax polyether-polyamide copolymers [31] has a CO<sub>2</sub> permeance of 1000 GPU (1000GPU=2.76 m<sup>3</sup>(STP)/(m<sup>2</sup>·h·bar)) with a CO<sub>2</sub>/N<sub>2</sub> selectivity of 40-50[32]. The membrane performance has been recently improved to reach a CO<sub>2</sub> permeance 2200 GPU and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 50 [33]. The Polyactive® (poly(butylene terephthalate)) has relatively low CO<sub>2</sub> permeability of 100-200Barrer [34], but the

**Table 2:** Representative polymers and inorganic fillers used for CO<sub>2</sub> selective MMMs.

Polymer matrix	Inorganic filler	Source
Poly(vinyl acetate) (PVAc)	Zeolite 4A, TiO <sub>2</sub>	[105-107]
Matrimid® 5218 and Ultem® 1000	Carbon molecular sieves, Zeolite	[108-111]
Poly(4-methyl-2-pentyne) (PMP)	Fumed silica, TiO <sub>2</sub>	[112, 113]
Matrimid	MOF-5	[114]
Polysulfone (PSf)	Silica	[115]
Poly(1-trimethylsilyl-1-propyne) (PTMSP)	Fumed silica, TiO <sub>2</sub>	[116]
Polyimide (PI)	Carbon nanotubes (CNTs)	[117]
Polymers of intrinsic microporosity (PIMs)	ZIF-8, CNTs	[118, 119]
poly(ethylene oxide) (PEO)	Graphene oxide	[120]
Pebax	1 D multi-walled carbon nanotube/graphene oxide nanoribbon	[121]
PIMs	metal-organic framework (MOFs)	[23]

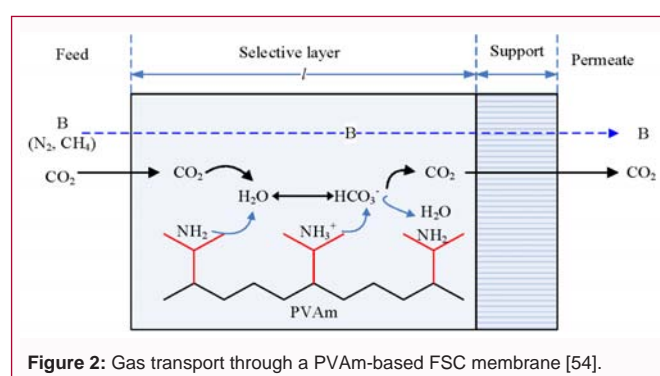


very thin nanocomposite membrane has been reported to achieve CO<sub>2</sub> permeance 2000 GPU with CO<sub>2</sub>/N<sub>2</sub> selectivity 60 [35]. Those investigation results indicated that extremely thin defect-free films of less than 50 nm thickness could be produced by dip-coating and scaled up successfully in future [26].

### Microporous organic polymers

Strong interests have been put on the development of microporous organic polymers (MOPs) due to its large surface area which can be comparable to the microporous inorganic materials such as zeolites and carbons. The representative MOPs include thermally rearranged (TR) polymers [36-39] and polymers of intrinsic microporosity (PIMs) [40-47]. The TR polymer membranes possess flexible structures to provide the easiness on module construction. Moreover, TR polymer membranes were also found to exhibit an excellent gas separation performance, especially for CO<sub>2</sub> related separation processes (e.g., CO<sub>2</sub>/CH<sub>4</sub> separation without any significant plasticization effects) [36] and also for high temperature H<sub>2</sub>/CO<sub>2</sub> separation in pre-combustion process [38]. However, most of efforts are still focused on preparation of lab-scale films of the TR polymer membranes, only a few literature reported the fabrication of hollow fiber TR membranes [48,49]. Kim et al. prepared the lab-scale TR-PBO hollow fiber membranes with a CO<sub>2</sub> permeance of 1938 GPU and a CO<sub>2</sub>/N<sub>2</sub> selectivity about 13 [49], and the selectivity obviously needs to be further improved to reach the industry attractive region.

Membranes made from polymers of intrinsic microporosity



attracted great interests due to their relatively slow physical aging, high gas permeability, as well as high selectivity compared to high free volume poly(1-trimethylsilyl-1-propyne) (PTMSP) membranes [45]. a TR membrane with high fractional free volume (22 - 24 %) was reported by McKeown et al. [50], which is comparable to PTMSP (32 - 34.3% [51,52]). Moreover, the functionalized PIMs with CO<sub>2</sub>-philic pendant tetrazole groups (TZPIMs) was reported to improve CO<sub>2</sub> permeance due to a strong interaction between CO<sub>2</sub> and N-containing organic heterocyclic groups by Du et al. [45]. Their results indicated that CO<sub>2</sub>/N<sub>2</sub> separation performance of TZPIMs can surpass the Robeson upper bound. Moreover, a systematic review on the preparation, characterization and application of PIMs has been conducted by McKeown [47]. They pointed out that composite membrane consisting of PIMs and other polymers showed a promising strategy for tailoring membrane properties to improve gas separation performance.

### Fixed-site-carrier membranes

Fixed-site-carrier (FSC) membranes for gas separation, especially for CO<sub>2</sub> removal from flue gas have attracted more attention due to its high CO<sub>2</sub> performance and high CO<sub>2</sub>/N<sub>2</sub> selectivity. The carriers (-NH<sub>2</sub>) are chemically bonded onto polymer matrix via covalent bonding. CO<sub>2</sub> can react with the amino functional groups when water is available, and transport through membrane by the combination of solution-diffusion (S-D) and facilitated transport (FT) mechanisms, while the other non-reactive gas species such as N<sub>2</sub>, O<sub>2</sub> can only transport via solution-diffusion as documented by Kim et al. [53]. A Schematic diagram for the gas permeation through a FSC membrane is shown in Figure 2 [54]. The gas flux of reactive component A (such as CO<sub>2</sub>) will be the sum of both solution-diffusion and carrier-mediated diffusion (i.e., facilitated transport), which can be expressed



as follows [53,55],

$$J_A = \frac{D_A}{l}(c_{A,o} - c_{A,l}) + \frac{D_{AC}}{l}(c_{AC,o} - c_{AC,l}) \quad (1)$$

where  $D_A$  and  $D_{AC}$  are diffusion coefficient of Fickian diffusion and carrier mediated (complex) diffusion, respectively, and  $l$  is membranes thickness of a selective layer. Feed pressure is crucial to get high flux by enhancing the contribution from both S-D and FT. However, after carrier saturation, further increasing feed  $\text{CO}_2$  partial pressure will not enhance the FT. Even though  $\text{CO}_2$  flux will continue increase due to S-D contribution, the trade-off between energy consumption and reduced membrane area (flux increase) should be identified to determine the optimal operating condition (ref. book chapter. modelling). Thus, a moderate feed pressure (e.g., 2.5-3bar) was recommended as the optimal operation condition of FSC membranes [56].

Table 1 shows some representative facilitated transport membranes that have been reported in the literature. Facilitated transport mechanism [57]. Among them, the Memfo group at NTNU patented a polyvinyl amine (PVAm)-based FSC membrane, and showed a very high  $\text{CO}_2$  permeance (up to  $5 \text{ m}^3 \text{ (STP)/(m}^2 \cdot \text{h} \cdot \text{bar)}$ ) and  $\text{CO}_2/\text{N}_2$  (>500) selectivity under humidified conditions [58]. This membrane is extremely promising for  $\text{CO}_2$  capture from flue gas in post combustion process where water vapor is usually involved in flue gas stream [56,58,59]. The use of ionic liquids (ILs) as carrier to transport  $\text{CO}_2$  in membrane separation processes is one of the fast growing research interests in the last years, and supported ionic liquid membranes (SILMs) are preferred to be used for  $\text{CO}_2$  separation due to their high selectivity and permeability as well as relatively good mechanical stability compared to conventional liquid membranes [60-65]. However, most of ionic liquids are still quite expensive.

### Mixed matrix membranes

Mixed matrix membranes (MMMs) comprise rigid permeable or impermeable particles, such as zeolites, carbon molecular sieves, silica and carbon nanotubes (CNTs), and disperse in a continuous polymeric phase to present interesting materials for improving separation performance of common polymer membranes [66]. Two types of inorganic fillers can be added into polymer matrix. MMMs with microporous fillers could improve selectivity based on molecular sieving or surface flow transport mechanism, and it might also to get an increased permeability if the preferred solid phase has a higher diffusion coefficient. While MMMs made from the adding of nonporous nanoparticles could improve gas permeability due to the increase of free volume. Chung et al. [67] reported that the properties for both polymer materials and inorganic fillers could affect the morphology and separation performance of MMMs. The rigid structure glassy polymers with high selectivity are more suitable for polymer matrix compared to rubbery polymers. However, the adhesion between glassy polymer phase and inorganic filler phase is a challenging issue for MMMs preparation. Moreover, the thermal and chemical stabilities of MMMs may suffer from the acid gases of  $\text{SO}_2$  or  $\text{NO}_x$  that are usually involved in flue gas. MMMs possess the higher mechanical strength compared to pure polymeric membranes, and a relatively low production cost compared to pure inorganic membranes. However, the main challenge for preparation of MMMs is to choose proper materials for both polymeric and inorganic phases to get a high gas separation performance and good compatibility. Examples for selection of polymer and inorganic filler for making  $\text{CO}_2$  selective MMMs are listed in Table 2.

## Membranes for $\text{CO}_2$ Capture in Power Plant

Gas membrane separation technology is an energy efficient and environmentally friendly process which has already been commercially used for many years in the selected gas purification processes such as air separation and natural gas sweetening [8,11], and judged to be an alternative and competitive next generation  $\text{CO}_2$  capture technology. Much effort is being put into the development of high performance membranes for this potential application, selected examples are given in the following references [4,12,13,18,49,58,68-72]. However, there are some challenges related to the limited application of a membrane system in post combustion  $\text{CO}_2$  capture. The flue gas in coal-fired power plant usually contains ca. 12-14 vol.%  $\text{CO}_2$  at a quite low pressure (i.e., a little over atmosphere pressure), which resulting in a very low feed  $\text{CO}_2$  partial pressure. Thus, the driving force for  $\text{CO}_2$  transport through a standard membrane system (i.e., a polymeric membrane based on solution-diffusion mechanism) will be very low without using feed compression and/or vacuum suction. Moreover, the chemical stability by exposure to the impurities such as  $\text{SO}_2$  and  $\text{NO}_x$  which usually exist in flue gas, may also be challenging related to membrane durability and lifetime. Therefore, a highly  $\text{CO}_2$  permeable, selective and chemically stable membrane at low cost is required for a membrane system to compete with other  $\text{CO}_2$  capture technologies, typically the benchmark amine absorption. The main focus on the development of membrane materials for post-combustion  $\text{CO}_2$  capture is to produce high performance membranes with long lifetime at a low cost. Three types of high  $\text{CO}_2$  selective membranes: 1) the FSC membranes, 2) the PolyActive™, and 3) the Polaris membrane were demonstrated on the pilot-scale.

The flat-sheet FSC membranes developed by the Memfo group at NTNU has been tested in EDP's power plant in Sines (Portugal) and E.ON's plant in Scholven (Germany) in 2011, and the membranes showed a stable performance over 6 months [73]. Late on, the hollow fiber FSC membranes were tested at Sintef  $\text{CO}_2$  lab at Tiller (Norway) with a flue gas produced from a propane burner. He et al. reported that single stage membrane system ( $8.4 \text{ m}^2$ ) can achieve >60% permeate  $\text{CO}_2$  purity at a feed and permeate pressure of 2bar and 0.2bar, respectively[74], and the system also showed quite fast response when changing feed  $\text{CO}_2$  composition. The reported pilot FSC membrane system provided great flexibility on testing the influence of process operating parameters, especially the operating temperature. But some challenges related to the module and process design should be further investigated. In December 2016, Air Products and Chemicals, Inc. licensed the technology and will bring the FSC membranes for post-combustion carbon capture to a higher technology readiness level (TRL), and the commercialization [75].

From the membrane material point of view, low pressure ratio (i.e., low feed pressure and low vacuum) is preferred to achieve high  $\text{CO}_2$  permeance for the FSC membranes. However, from the engineering point of view, a relatively high pressure ratio (increasing driving force) will give higher  $\text{CO}_2$  flux, and reduce the required membrane area. It is however important to balance this against the operating conditions where the facilitated transport can be the advantage. Thus, the trade-off between capital expenditure (CAPEX) related to the required membrane area and the operation expenditure (OPEX) related to power consumption of driving equipment) needs to be well balanced. He et al. [56,59,76] and Hussain et al. [77] conducted the process feasibility analysis by HYSYS integrated with an in-house membrane program (ChemBrane, developed by

Grainger [78]) to investigate the influence of process parameters on energy demand and flue gas processing cost using the CO<sub>2</sub>-selective FSC membranes. Their results showed that membrane process using a high performance FSC membrane was feasible for CO<sub>2</sub> capture, even with a low CO<sub>2</sub> concentration (~10%) in the feed flue gas, compared to the amine absorption in terms of the energy requirement, and it was possible to achieve >90% CO<sub>2</sub> recovery and a purity above 95% CO<sub>2</sub> in permeate stream.

The Poly Active™ membranes developed by Helmholtz-Zentrum Geesthacht was tested for CO<sub>2</sub> capture from real flue gas in the pilot scale with a membrane area of 12.5m<sup>2</sup> [22]. The membrane system also showed stable performance with permeate CO<sub>2</sub> purity 60-70mol. % over 740h continuously. They reported that membrane processes using PolyActive™ membranes seem to be well suited for post combustion CO<sub>2</sub> separation, and a CO<sub>2</sub> purity 68.2 mol.% in the permeate and a recovery of 42.7% can be achieved at the tested condition in single stage process.

The Polaris® membranes developed by Membrane Technology & Research, Inc. (MTR) has been demonstrated on the pilot scale for CO<sub>2</sub> capture from a natural gas combined cycle (NGCC) power plant [79]. A 20 TPD skid was tested to validate the advanced modules (multi-tube and plate-and-frame) designed for low pressure drop and small footprint, and the system showed quite stable performance over ca. 1000hrs [80]. MTR patented their process by feeding high CO<sub>2</sub> content air stream (air as sweep gas in the permeate side of the 2<sup>nd</sup> stage membrane unit) into the boiler to increase the CO<sub>2</sub> concentration in the flue gas [81], which can potentially reduce the energy consumption by avoiding the vacuum pump. However, how the CO<sub>2</sub> contained air influences the boiler operation should be further tested.

Merkel et al. [32] also pointed out that improving membrane permeance is more important than increasing selectivity (if selectivity >30) to further reduce the cost of CO<sub>2</sub> capture from flue gas. They reported that membrane with a CO<sub>2</sub>/N<sub>2</sub>selectivity above 50 and a 4000GPU CO<sub>2</sub>permeance could offer a capture cost below 15 \$/tonne CO<sub>2</sub>, which is lower than US Department of Energy's (DOE) target goal of 20\$/tonne CO<sub>2</sub> [82]. Even though the required high performance membrane has not yet been achieved, their researches emphasized quantitatively the need to improve the present membranes to realize a purely membrane-based process for CO<sub>2</sub> capture. Therefore, this environmentally friendly technique with further improved membrane performance could promote the membrane systems as a promising candidate for CO<sub>2</sub> capture from flue gas in post-combustion process if the above-mentioned challenges can be well addressed.

## Membranes for CO<sub>2</sub> Capture from Process Industry

### CO<sub>2</sub> capture from cement factory

Cement factory represents 7% of global anthropogenic CO<sub>2</sub> emissions and is therefore pursuing solutions for carbon capture from high CO<sub>2</sub> content (ca. 17 vol.% wet base) flue gas. Application of carbon capture and storage (CCS) from cement kilns would have great potential to reduce CO<sub>2</sub> emission from this industry, but will naturally also influence the cement production costs. Thus, the European cement industry (through Heidelberg Cement) is taking big interest in low-cost CCS technologies.

The cement production releases greenhouse gas emissions both directly and indirectly: the heating of limestone (calcination) releases

CO<sub>2</sub> directly, which accounts for ~50% of all CO<sub>2</sub> emission in cement production; the burning of fossil fuels to heat the kiln indirectly results in CO<sub>2</sub> emissions. Employment of CCS is considered as one of the most important techniques to achieve the Norcem Zero CO<sub>2</sub> Emission Vision 2030 – a test site for carbon capture technologies is placed in Brevik, Norway, and funding of this project is mainly provided by the CLIMIT program in Norwegian Research Council. The project in Brevik was launched 2013 to test process feasibility with four different technologies (amine absorption, membranes, solid adsorbent, and chemical looping). This is the first pilot-scale membrane system tested in a cement factory [83], and the PVAm based flat-sheet FSC membranes (developed by Memfo team at NTNU) for CO<sub>2</sub> capture from a 17 vol.% (wet base) CO<sub>2</sub> flue gas was chosen. Many challenges related to the process and module design were revealed, and it was difficult to achieve a stable and high performance membrane system, but a CO<sub>2</sub> purity up to 72 vol.% was achieved for short periods when all process parameters were well controlled in the single stage FSC membrane system [84]. However, the membrane efficiency in the plat-and-frame module was quite low, and the designed system suffered water condensation /corrosion issues. Thus, hollow fiber FSC membrane modules with a pilot membrane area of ca. 20m<sup>2</sup> was constructed by the joining force from Air Products and Chemicals, Inc. in 2016, and tested at Norcem, Brevik [85]. The FSC membrane system was evaluated to be at “Technology readiness level” (TRL) level 5 (EU-definition). The system showed stable performance over 6 months at different conditions even at high NO<sub>x</sub> and SO<sub>2</sub> loading (average 100ppm and 5ppm, respectively) flue gas. They reported that stable permeate CO<sub>2</sub> purity of 65 vol.% over the accumulated 24 days was achieved[20]. Techno-economic feasibility analysis was also conducted to achieve 80% CO<sub>2</sub> recovery and >90vol.% CO<sub>2</sub> purity. However, the designed two stage membrane system might be difficult to achieve high CO<sub>2</sub> purity (>95 vol.%) requirement for enhanced oil/gas recovery (EOR/EGR) (especially the O<sub>2</sub> limitation). The potential solutions are to introduce a third stage membrane unit or a low-temperature liquefaction unit. The CEMCAP project under EU H2020 looked into the membrane-assisted CO<sub>2</sub> liquefaction process for CO<sub>2</sub> capture in cement factory [86], which might provide an energy efficient solution. However, such investigation is still in the early conceptual design phase.

### CO<sub>2</sub> capture from other industries

Iron and steel production industries are quite large energy consuming manufacturing sectors around the world, and CO<sub>2</sub> emissions from these manufacturing sectors represent about 10 % of total global CO<sub>2</sub> emissions [1]. CO<sub>2</sub> capture in power plants has received a lot of attention as described in Section 3, but very little attention has been put on CO<sub>2</sub> capture from iron and steel production plants so far. There are only a few studies reported on CO<sub>2</sub> capture in iron and steel production industries [87-90]. Membrane technology could be favorable to be used in steel making industries as reported by Favre et al. [91]. The Ultra Low CO<sub>2</sub> Steelmaking (ULCOS) project was launched in 2004 to develop a new steel production technology that could drastically cut CO<sub>2</sub> emissions to 50% by 2030. The PVAm based fixed-site-carrier (FSC) membranes was tested for CO<sub>2</sub> capture from synthetic nitrogen free blast furnace (NFBF) exhaust gases (N<sub>2</sub>/CO<sub>2</sub>/CO/H<sub>2</sub>: 10%/36%/47/7%) [90], and the results indicated that the FSC membranes could be a potential candidate for CO<sub>2</sub> capture from flue gas in the steelmaking industry. However, no membrane material has been tested for CO<sub>2</sub> capture from real exhaust gas in steel/iron industry.

## Conclusions and Future Perspectives

Even though there are many types of membrane materials developed in the literature for CO<sub>2</sub>/N<sub>2</sub> separation, only the PVAm based FSC membrane, the PolyActive™ membrane and the Polaris™ membrane have been tested on the pilot scale post-combustion CO<sub>2</sub> capture. Each type of membrane has its own advantages on the material property and processability, and challenges on engineering design of module and process (especially the pre-treatment) for commercialization. Further development is required to reach higher TRL level, and two/multi-stage membrane systems should be designed, constructed and tested in the real flue gas to achieve the separation requirement related to CO<sub>2</sub> purity and CO<sub>2</sub> recovery. The lifetime of membrane materials should also be documented over long time. Nevertheless, gas separation membrane systems could be an energy efficient and environmentally friendly technology for post-combustion CO<sub>2</sub> capture in the near future by the joint force from membrane science and engineering.

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