

The application of membrane technology to post-combustion separation of carbon dioxide from coal-fired power plant flue gas

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Matthew received his BSc(Hons) (2008) and PhD (2012) in inorganic chemistry at the University of Otago. Since 2012 he has worked as a postdoctoral associate at the University of Colorado Boulder, split between the Chemistry and Chemical Engineering Departments. During this time he was part of the academic-industrial team which successfully completed a \$3.8 million DOE ARPA-E project relevant to post-combustion carbon dioxide capture by producing the ~6000 GPU membrane described in this article. He has also taken part in numerous collaborative projects regarding materials for olefin/paraffin separation, magnetic alignment of lyotropic liquid crystals, metal-ion-containing ionic liquids, materials for carbon dioxide/methane separations, and barrier materials for chemical warfare agents. Matthew is currently working on a second DOE ARPA-E project related to carbon dioxide/nitrogen separation technology. His future research interests include fundamental and directly applicable science in the field of inorganic/organic materials chemistry.

The convenience and cost of coal power

Coal-fired power plants are extremely useful sources of electricity. Coal is an abundant and cheap source of energy for electricity generation. It has relatively few alternate uses when compared to other fossil fuels such as petroleum and natural gas. Coal-fired power plants can be located close to areas of major electricity consumption, like population or industrial centres, to minimise losses or interruptions in the transmission of electricity. Furthermore, coal-fired power plants are reliable and their output can be increased at short notice, allowing them to cope with surges in demand.

New Zealand is fortunate to have significant sources of renewable energy, including wind, geothermal, and hydroelectric.¹ However, the Huntly power plant plays a strategic role in meeting electricity needs, responding to surges in demand, and avoiding transmission losses. The Huntly plant runs using a mixture of coal and natural gas and is capable of generating 20% of NZ's electricity needs, but in doing so produces over 50% of New Zealand's carbon dioxide gas emissions from electricity generation. The coal units at Huntly were estimated to produce 1600 kT of CO₂ in 2010,² approximately 5% of New Zealand's total CO₂ emissions for that year.³ If Huntly were an average, 600 MW_e coal-fired power plant (which it is not),⁴ it would emit 11,000 tons of CO₂ per day⁵ - approximately 13% of New Zealand's total CO₂ emissions in 2010.³

Globally, coal plays a much greater role than it does in New Zealand. Many industrialised and developing countries are heavily reliant on coal for electricity generation. Incidentally, countries with some of the largest coal deposits are also the highest emitters of CO₂. These are China (25%), the United States (16%),⁶ and India (6%) - accounting for 47% of total world CO₂ emissions in 2010 (Fig. 1).³ A 2007 study led by the Massachusetts Institute

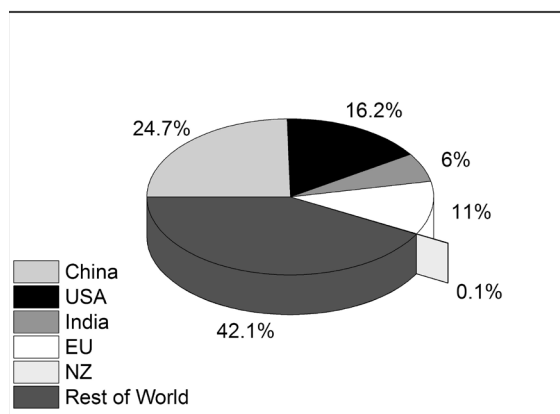


Fig. 1. The relative contributions of countries to global CO₂ emissions in 2010³

of Technology determined that CO₂ emissions from coal-fired power plants account for almost 40% of annual global anthropogenic CO₂ emissions.⁷

Research on climate change and ocean acidification has made it abundantly clear that there will be significant environmental, economic, and social costs to generating and releasing large amounts of CO₂ into the atmosphere.⁸ Being able to separate and capture CO₂ from large point sources, such as coal-fired power plants, would significantly slow the rate that anthropogenic CO₂ is released into the atmosphere. This would help to alleviate, or at least delay, the worst effects of climate change.

From a political standpoint, it is difficult to reconcile the clash between socioeconomic and environmental factors. Socioeconomic concerns are immediate, in that people want to use a lot of electricity in the present, and the consequences of a lack of electricity are obvious. In contrast, environmental factors are diffuse, intangible, futuristic, even overwhelming. This makes them difficult to conceptualise, understand, and appreciate.

The largest reduction in CO₂ emissions would be accomplished by a significant change in human behaviour. However, without an immediate and easily-understandable threat, dramatic changes are unlikely to occur. Alternatively, the development of a technological solution to the problem is particularly desirable. This would result in minimal increases to electricity availability and price, while significantly reducing CO₂ emissions. Allowing such 'consequence free' growth would neither impose economic pressure on, nor necessitate significant behavioural changes by, the average person.

The availability of an economically viable technological solution may provide the impetus for international political action with tangible outcomes. Hopefully, a legally binding international agreement to reduce CO₂ emissions will be reached during the United Nations Framework Convention on Climate Change meeting in Paris in November-December 2015. It is likely that consideration of *how* any agreed targets will be achieved will play an important role in the formulation of any agreement.

Since coal-fired power plants are responsible for such a large proportion of global CO₂ emissions, it would be sensible to design a CO₂ capture technology with that application in mind. So, where could an economically viable technology for limiting CO₂ emissions fit into a coal-fired power plant?

Options for CO₂ capture

Currently there are three proposed strategies for capturing CO₂ from a coal-fired power plant.⁷ *Oxy-fuel combustion* requires separating oxygen from air (mainly nitrogen). Burning coal with 95% O₂ would result in CO₂ being the major product of combustion, making it easy to capture. *Pre-combustion capture* requires converting coal into hydrogen and CO₂, then removing the CO₂ before burning the hydrogen to generate electricity. *Post-combustion capture* would mean that coal is burnt as normal and the CO₂ is then separated from a waste stream (*flue gas*) composed largely of N₂ (Table 1).

Table 1. Example gas compositions for coal-fired and natural gas power plants

Component	Coal-fired power plant flue gas (%)	Natural gas power plant flue gas (%)
N ₂	77	74
CO ₂	13	8
H ₂ O	6	14
O ₂	4	4
NO _x	420 ppm	70 ppm
SO ₂	420 ppm	N/A
CO	50 ppm	300 ppm

In principle, a *post-combustion* capture system can be retrofitted into existing plants and plant designs. Retrofitting is less costly and faster to implement than the alternate technologies which would require major alterations to process and plant designs.

For the *post-combustion capture* of CO₂, the United States Department of Energy (DOE) has set 'cost for capture'

targets of \$40 per ton of CO₂ by the year 2020-2025 and \$10 per ton of CO₂ by the year 2030-2035.⁹ Membranes are one technology that could be applied to achieving these goals, so let's discover what they are and how they could be used.

How membranes work

For the purpose of this article, a membrane will be defined as a material used to partition two volumes. In practice, a membrane will be made of a 'selective' or 'active' layer, comprised of a dense polymeric material, typically 100 to 1000 nm thick (Fig. 2). The active layer is referred to as the *membrane material* and is responsible for separating different gases. Because the active layer is so thin, it sits atop a porous support to provide the membrane with mechanical strength.

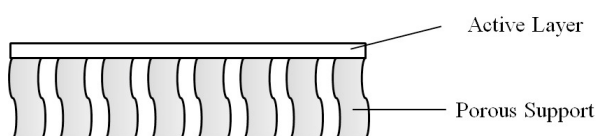


Fig. 2. A cartoon representation of a composite membrane

A membrane can be thought of as a doorway between two rooms, but on a molecular scale that analogy is not correct. In dense polymeric membranes, transport through the membrane occurs via the solution-diffusion mechanism (Fig. 3).¹⁰ To get from one volume, the *feed side*, to the other volume, the *permeate side*, gas *i* must cross the membrane. To do so, it dissolves into the membrane at the feed side. The gas molecule then diffuses across the membrane,¹¹ driven by a concentration gradient such as partial pressure. Upon reaching the permeate side, gas *i* will desorb from the membrane and escape into the permeate volume.

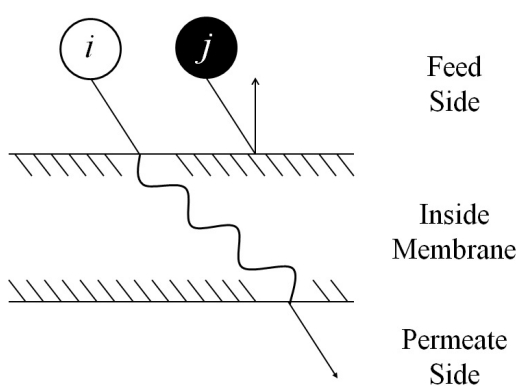


Fig. 3. A simplified depiction of gas *i* moving across a dense polymeric membrane by the solution-diffusion mechanism. It is important to note that gas *j* will actually move across the membrane using the same mechanism as gas *i*, albeit at a significantly slower rate. Modified from reference 12.

Important membrane properties

The defining features of a membrane are *permeability*, *permeance*, and *selectivity*.¹³

Permeability reflects the ability of a gas to transport through the active layer. Permeability always refers to a specific gas, therefore will be written as "the permeability of gas *i* is...". As shown in Equation 1, permeability

reflects the ability of a gas to dissolve into the material (solubility) and diffuse through it (diffusivity). Permeability is typically reported in units of 'barrier',¹⁴ named after New Zealander Dr. Richard M. Barrer.

Permeance describes the rate at which a gas moves across a membrane area. This means that membranes with high permeance will process gas faster, or require less membrane area, than a membrane with low permeance. As can be seen in Equation 2, a higher permeance membrane can be obtained by reducing the thickness of the active layer. Permeance is typically reported in 'Gas Permeation Units (GPU)'.¹⁵

Selectivity is the ratio of how permeable the material is to two different gases (in this case *i* and *j*). *Ideal selectivity* refers to the permeability ratio of two different gases when they are tested *individually*, i.e. as single gas measurements, rather than as a mixture of gases.

$$\text{Permeability}_i = \text{Diffusibility}_i \cdot \text{Solubility}_i \quad (1)$$

$$\text{Permeance}_i = \frac{\text{Permeability}_i}{\text{Active Layer Thickness}} \quad (2)$$

$$\text{Selectivity } (\alpha_{i/j}) = \frac{\text{Permeability } (i)}{\text{Permeability } (j)} \quad (3)$$

Equations 1-3. The *permeability* of gas *i* is described as the product of its diffusivity and solubility coefficients inside the membrane material. The *permeance* of gas *i* is determined by the permeability and thickness of the membrane material. The *selectivity* of a membrane is determined by the relative permeabilities of gases *i* and *j*.

To apply a membrane in the real world, other factors also need to be considered.¹² For example, can the material be processed into defect-free thin (ca. 100 nm) films, are the properties of the thin film the same as a thick film, how does the material perform with a mixed-gas or 'real' feed, is the membrane physically and chemically stable enough to retain performance over time, and is the material expensive to make?

For the moment, we shall ignore these rather pressing issues. What then are the *permeance* and *selectivity* properties required to economically separate CO₂ from flue gas?

Membrane requirements for separating CO₂ from flue gas

When considering the application of any academic idea to the real world, or perhaps even before starting to generate ideas, it is important to consider what the real world actually needs.

In 2010, the 'Membrane Technology and Research company' (MTR) published a definitive article evaluating the applicability of several membrane process designs to the capture of CO₂ flue gas from coal-fired power plants.⁵

Fig. 4 shows MTR's modelling results for the best of the multi-stage processes they considered. They demonstrate the effect of increasing CO₂/N₂ selectivity on the cost of CO₂ capture for three potential membranes with permeances of 1000, 2000, and 4000 GPU, respec-

tively. It is interesting to note that the cost of capture is much lower when the permeance of the membrane is increased, but levels off after a CO₂/N₂ selectivity of 30.

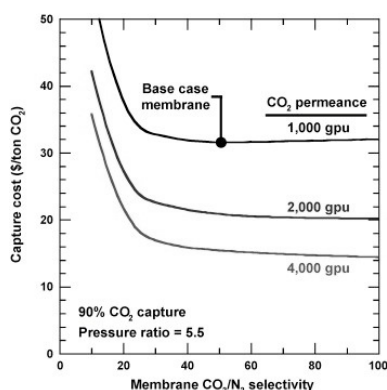


Fig. 4. The effect of membrane *permeance* and *selectivity* on the cost of capturing CO₂ from the flue gas of a coal-fired power plant⁵

Using the conditions MTR assumed for processing flue gas, the *maximum* possible concentration of CO₂ on the permeate side is 73 mol%.^{16,17} This is true *no matter how selective the membrane is!* But, because 27 mol% of N₂ must also be collected, and the permeance of N₂ is inversely proportional to the selectivity, a larger membrane area will be required to permeate the N₂. Therefore, as the selectivity of the membrane approaches infinity so does the amount of membrane area required. That would be quite expensive!

The levelling off of capture costs with increasing selectivity therefore represents the compromise between a more efficient process and increasing the amount of membrane area required to treat the gas.¹⁸

In conclusion, we know that *high CO₂ permeance* is the key parameter for achieving economic CO₂ separation from flue gas. It implies that modest CO₂/N₂ selectivities of 20-40 are acceptable and that CO₂/N₂ selectivities over 30 will make little difference to the cost of CO₂ capture.

Now that we have an idea of our criteria, are there any membranes which could achieve our goals?

State-of-the-art membrane technology

When assessing state-of-the-art technology it is important to consider where the technology lies along its developmental pathway. This is because companies, which are quaquary by nature, need to balance the financial risk of paying to adopt a new technology against the potential economic value that technology could provide. In the case of CO₂ capture from flue gas, the risk would be in a technology unproven to operate over a financially justifiable period, and the economic value in adopting membrane technology could be in avoiding legislatively imposed penalties or fines for releasing CO₂ into the atmosphere. To contextualise the development pathway of membrane technology for an example post-combustion CO₂ capture process, a flow chart is presented in Fig. 5.

Recently, a collaboration between the University of Colorado Boulder and the 3M Company produced a membrane with a permeance of 6100 ± 400 GPU and a CO₂/

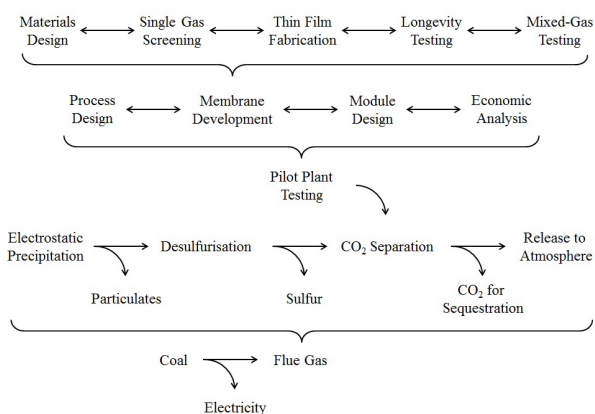


Fig. 5. A brief consideration of where membrane technology could fit into an example post-combustion CO₂ capture process and the developmental pathway required to make that a reality

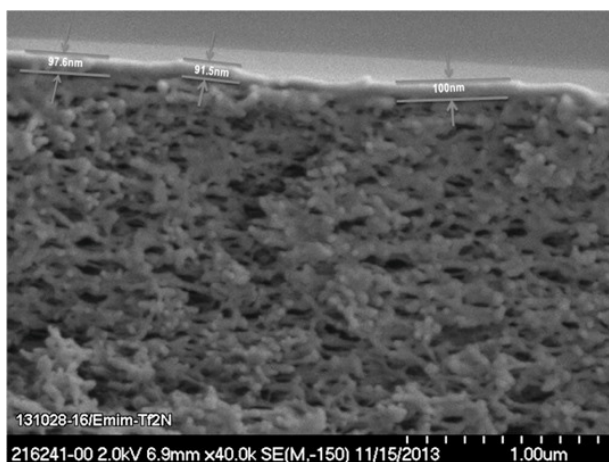


Fig. 6. A scanning electron microscope (SEM) image of a membrane showing the $96 \pm 4 \mu\text{m}$ active layer on top of a porous support. Reprinted with permission from *Ind. Eng. Chem. Res.*, 53 (51), 20064-20067. Copyright 2014 American Chemical Society.¹⁹

N₂ selectivity of 22 ± 2 - corresponding to a potential capture cost of \$15 per ton of CO₂.¹⁹ This membrane has an approximately 100 nm thick active layer comprised of ionic liquid and poly(ionic liquid) (Fig. 6), prepared using a two-step coating process.²⁰ The preparation of this membrane is a significant achievement, but it is at a very early stage of development.

MTR currently has a set of membranes named 'Polaris™' going through pilot plant testing.²¹ The composition of Polaris™ is a closely guarded secret. The original 'Polaris™' has a CO₂ permeance of 1000 GPU and a CO₂/N₂ selectivity of 50 - corresponding to a potential capture cost of \$30 per ton of CO₂. In 2014, an advanced iteration of Polaris™ was disclosed to have a CO₂ permeance of 3000 GPU and a CO₂/N₂ selectivity of 50 - corresponding to a potential capture cost of \$20 per ton of CO₂.²² These capture costs are well under the DOE target of \$40 per ton of CO₂ by the year 2020-2025.

In 2010, a pilot-scale membrane unit containing the original Polaris™ was reported to have lasted for 45 days of continuous operation at the Cholla power plant in Arizona with no decrease in performance.²¹ In 2014, a second generation Polaris™ membrane (2000 GPU) was reported to have 60-70% increased capacity over the first genera-

tion system.²² These results are extremely promising and hopefully this technology will soon be available for commercialisation.

What to do with the captured CO₂?

Assuming that separation technologies are successfully developed and implemented, what can be done with the captured CO₂? Worldwide there are options like burying the CO₂ in stable geological formations deep within the earth, such as depleted natural gas reservoirs, or using CO₂ to enhance oil recovery from petroleum wells.

What would be good options for New Zealand?

Perhaps the Maui gas fields would provide a suitable site for CO₂ sequestration? However, the geology of New Zealand is relatively volatile and it is difficult to predict the long-term stability of deep sites. Should leaks occur from a deep sea site like Maui would it be worse to have directly injected CO₂ into the ocean rather than releasing it into the atmosphere?

Recycling CO₂ for applications such as carbonation of drinks, fire extinguishers, and synthesis of chemical feed stocks seems like an attractive option. Perhaps an effective solar and algae-based process can be developed to recycle CO₂ into biofuels? However, recycling would likely only account for a small fraction of the total CO₂ produced and may or may not add feasibility to the economics of CO₂ capture.

Outlook

Contrasting the convenience of coal-fired power plants with the consequences of climate change and ocean acidification paints an unattractive picture. Similarly, the juxtaposition of immediate and futuristic socioeconomic consequences presents a difficult political problem.

In this context, a technological development that will delay or mitigate future environmental, economic, and social consequences, but avoid imposing significant socioeconomic penalties in the present, is a very attractive option.

Membrane technology appears to be a promising candidate in the short-term. However, CO₂ emissions are just one contributor to global climate change, and climate change is just one problem facing the world. How humanity faces its problems and advances culturally and technologically will be determined in part by your choices and actions. Sometimes the choice to do nothing will have the most significant impact of all - so choose wisely and act courageously. Ka kite anō.

Acknowledgements

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15. $1 \text{ GPU} = 1 \times 10^{-6} (\text{cm}^3_{\text{gas i}} (\text{STP})) / (\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}) = 0.33 \times 10^{-15} (\text{mol}_{\text{gas}}) / (\text{m}^2_{\text{area}} \cdot \text{s} \cdot \text{Pa}_{\text{gas}})$.
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