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Membrane-assisted CO₂ liquefaction: performance modelling of CO₂ capture from flue gas in cement production

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Abstract

CEMCAP is an international R&D project under the Horizon 2020 Programme preparing the ground for the large-scale implementation of CO₂ capture in the European cement industry. This paper concerns the performance modeling of membrane-assisted CO₂ liquefaction as a possible retrofit application for post combustion CO₂ capture. For the relatively large CO₂ concentrations that are typical for the flue gas in conventional cement kilns, it may be possible to capture CO₂ by combining a single membrane unit for bulk separation and a CO₂ liquefaction train in which the waste stream is recycled and mixed with the feed to the membrane system. The required membrane surface area is strongly correlated with the CO₂ concentration in the cement kiln flue gas, as well as targeted CO₂ recovery, pressure ratio across the membrane, membrane separation factor and CO₂ permeance. Specifications for flue gas pre-conditioning and an overall techno-economic evaluation are planned to follow the evaluation of experimental results for membrane performance under realistic conditions, as well as for CO₂ liquefaction performance.

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1. Introduction

CEMCAP is an international R&D project under the Horizon 2020 Programme preparing the ground for the large-scale implementation of CO₂ capture in the European cement industry [1]. The four technologies studied are oxyfuel combustion, retention of CO₂ from fluegas in a chilled ammonia solution, calcium looping where CO₂ from flue gas reacts with CaO particles to form CaCO₃, and membrane-assisted CO₂ liquefaction. Assessment of pilot-scale test results and the iteration of experimental and analytical research for these technologies will provide a strategic techno-economic decision basis for CO₂ capture in the European cement industry.

Membrane-assisted CO₂ liquefaction is based on the principle of combining two different separation technologies, both of which are not perfectly suited for stand-alone capture of CO₂ at low concentration in flue gases. In the combined separation process, each technology can carry out a partial separation within its favorable regime of operation. Polymeric membranes are generally suited for bulk separation of CO₂ with moderate product purity. The low-temperature separation is very well suited for purification of CO₂ from a gas stream with moderate to relatively high CO₂ concentration in order to obtain a high-purity CO₂ product stream through condensation of CO₂ and removal of the volatile components nitrogen, oxygen etc. by phase-separation. A significant advantage for the principle of membrane-assisted CO₂ liquefaction is that there is no requirement for process steam, which is normally unavailable in cement factories. The process will in principle depend on electric power only, which is readily available in most cases.

In the present work the performance modelling effort related to membrane-assisted CO₂ liquefaction, the interaction between the membrane separation system and CO₂ liquefaction, and the optimization of process conditions and the system requirements, are presented. A general overview of the post-combustion technology of membrane-assisted CO₂ liquefaction is given in figure 1. The flue gas from a conventional cement kiln has a CO₂ concentration typically in the range of 14-35 % [2] and is available at atmospheric pressure and elevated temperature. The flue gas is pre-conditioned before entering the membrane system. With a CO₂ selective membrane system, the exhaust is depleted in CO₂, and the concentration in the permeate is increased to a level sufficient for recovery and purification by liquefaction. After liquefaction the captured CO₂ is in liquid phase at high purity, and can thus be pumped to dense-phase transport pressure.

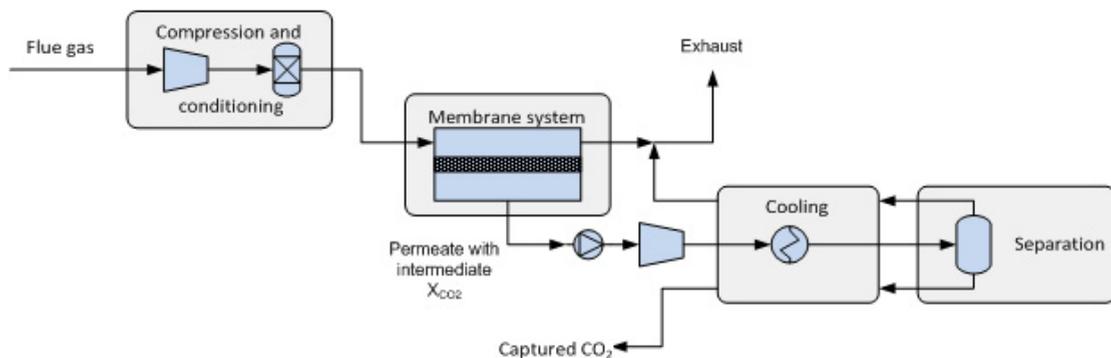


Fig. 1. Simplified process scheme for membrane-assisted CO₂ liquefaction.

First the modelling results of the membrane separation and liquefaction as stand-alone processes are presented, followed by the iterative modelling results where the purged gas from the liquefaction is added to the feed stream entering the membrane system.

Nomenclature

f	CO ₂ mole fraction in feed towards liquefaction unit
p	pressure, Pa
x	mole fraction at feed side membrane, -
\bar{x}	average mole fraction at feed side membrane, -
x	mole fraction at permeate side membrane,
A	membrane area, m ²
CCR	CO ₂ capture ratio, -
L	membrane thickness, m
P	permeability, m ³ (STP)m/(m ² sPa)
P/L	permeance, m ³ (STP)/(m ² sPa)
Q	flow, m ³ /s
X	CO ₂ mole fraction liquid phase in phase separation
Y	CO ₂ mole fraction vapour phase in phase separation
$\alpha_{\text{CO}_2/\text{N}_2}$	ideal separation factor of CO ₂ and N ₂ , -
ϕ	pressure ratio, -

Indices

f	feed
p	permeate
r	retentate

2. Membrane separation

The membrane system in this retrofit cement manufacture application is modelled as a single module to pre-concentrate the CO₂ for liquefaction, see Fig 2. The system is characterized by feed conditions (exhaust flow Q_f and CO₂ concentration from cement plant $x_{\text{CO}_2,f}$), membrane performance (ideal separation factor $\alpha_{\text{CO}_2/\text{N}_2}$ and permeance P/L), system parameters (feed pressure p_f and permeate pressure p_p , and membrane area A). Here the flue gas is assumed to consist of only CO₂ and N₂. The presence of other components in the flue gas and above all the effect of relative humidity is acknowledged and will influence the membrane separation. However, sufficient and reliable permeability data at conditions for the intended application are not available from literature and therefore results from this study will be used to set the conditions for experimental determination of CO₂, N₂ and H₂O permeabilities at relevant range of feed compositions, pressure and temperature.

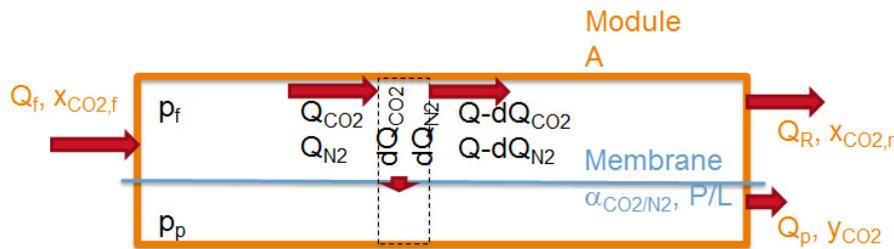


Fig. 2. Schematic of membrane system showing the base case for retrofit application.

Membrane performance data related to separation of carbon dioxide and nitrogen and a so-called "upper bound" correlation of ideal separation factor and permeability are presented in "Robeson plots" [3]. The ideal separation factor [4] $\alpha_{\text{CO}_2/\text{N}_2}$ is defined as the ratio of CO₂ and N₂ permeabilities, and relates the mole fractions y in the permeate to the mole fractions x in the feed, in case of a perfect vacuum at the permeate interface of the membrane.

The pressure on the feed side will be at atmospheric pressure or above, and on the permeate side near vacuum. The actual separation performance is constrained by upward practical feed-to-permeate pressure ratio (ϕ) levels, and is evaluated by the Rautenbach model in equation (1), see [5].

$$y_{CO_2} = \frac{1}{2} \left(1 + \phi \cdot \left(x_{CO_2} + \frac{1}{\alpha_{CO_2/N_2} - 1} \right) \right) - \sqrt{\left(\frac{1}{2} \left(1 + \phi \cdot \left(x_{CO_2} + \frac{1}{\alpha_{CO_2/N_2} - 1} \right) \right) \right)^2 - \frac{\alpha_{CO_2/N_2} \phi x_{CO_2}}{\alpha_{CO_2/N_2} - 1}} \quad (1)$$

Figure 3 shows the minimum requirements for the CO₂/N₂ ideal separation factor and membrane pressure ratio, for indicated CO₂ mole fractions in the feed representative of flue gases in cement industry (0.15, 0.25 and 0.35) and in the permeate as expected to be near the optimum for follow-on liquefaction (0.55, 0.65 and 0.75). It is concluded from this figure that a membrane material with a CO₂/N₂ separation factor $\gg 10$ is required, and the membrane separation process is carried out at a pressure ratio of at least 5 and preferably more than 10. According to [3], membrane materials are available that comply with the ideal separation factor criterion with the majority of membranes having α_{CO_2/N_2} in the range 10 to 40. Note that the Rautenbach model applies to the local conditions on both sides of the membrane, and does not consider depletion of the CO₂ along the membrane module.

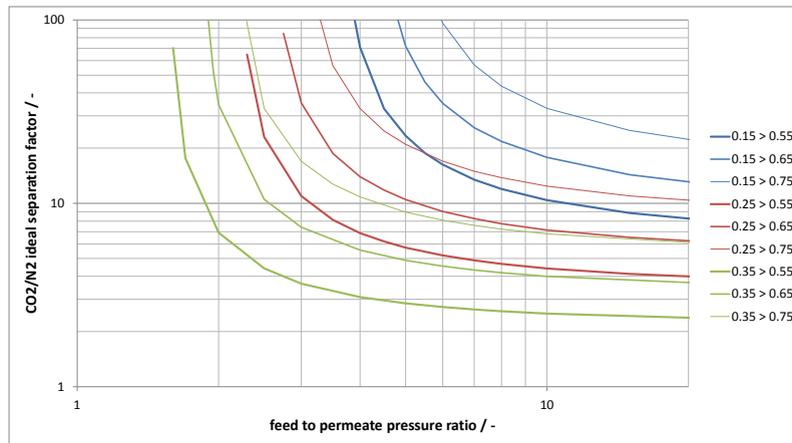


Fig. 3. Minimum requirement for membrane ideal separation factor and pressure ratio, according to Rautenbach model. Curves are representative for fixed feed and permeate molar CO₂ fractions.

The performance of the membrane system in figure 2 is fully described by the Rautenbach model and the following equations (2), (3) and (4). The requirement for CO₂ recovery of the membrane system is now accounted for as well as the non-constant driving for permeation along the length of the membrane module, which directly influences the minimum membrane area A . The logarithmic mean mole fraction is used to describe the effective feed concentration for the cross-flow module assuming a well-mixed permeate [6].

$$Q_{CO_2,r} = \left(1 - \frac{\text{desired } CO_2 \text{ recovery}}{100\%} \right) Q_{CO_2,f} \quad (2)$$

$$\bar{x}_{CO_2,f} = \frac{x_{CO_2,f} - x_{CO_2,r}}{\ln(x_{CO_2,f}/x_{CO_2,r})} \quad (3)$$

$$A = \frac{Q_{CO_2,p}}{(P/L)_{CO_2}(\bar{x}_{CO_2,f} p_f - y_{CO_2} p_p)} \quad (4)$$

3. Liquefaction

The stand-alone CO₂ capture ratio (CCR) for the CO₂ liquefaction unit follows from CO₂/N₂ vapour-liquid equilibrium data and depends strongly on the pressure and temperature in phase separation. Typical conditions in liquefaction are 20-40 bar and temperatures down to around -55°C. The base case process configuration is shown in figure 4. After vacuum pumping the permeate is assumed to undergo three-stage compression with intercooling and water knock-out after each compression stage, and a final mol sieve polishing stage for dehydration. Further, the gas is assumed to be cooled by internal heat recuperation and auxiliary refrigeration, resulting in partial CO₂ condensation. The liquid CO₂ is separated from the CO₂-depleted gas phase by phase separation and is subsequently pressurized by CO₂ pumping.

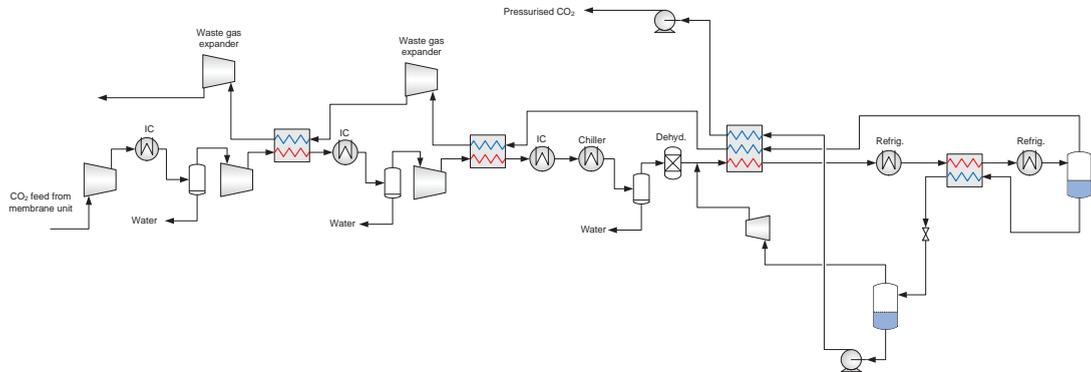


Fig. 4. Base configuration for low-temperature CO₂ condensation.

The vapour-liquid equilibrium for the binary CO₂/N₂ mixture is shown in figure 5. The CCR is calculated from the CO₂ mole fraction X and Y in liquid and vapour phase respectively, and f the mole fraction in the feed towards the liquefaction unit, see equation (5). Figure 6 shows the separation pressure required to achieve a certain CCR at a condensation temperature of -55 °C, and for CO₂ feed fractions in the range 0.50 to 0.65.

$$CCR = \frac{X}{f \left(1 + \frac{X-f}{f-Y} \right)} \quad (5)$$

The specific work to capture CO₂ by liquefaction is calculated for various CCR and different CO₂ feed concentrations, see figure 7. It is obvious that the specific work decreases with increasing CO₂ feed concentration. There is however a minimum in specific work, and this minimum shifts towards higher CCR with increase in CO₂ feed concentration, leaving room for optimization by recycling CO₂ to the membrane separation unit.

4. Membrane-assisted CO₂ liquefaction

In the model of membrane-assisted CO₂ liquefaction the CO₂ recovery module of figure 2 and liquefaction unit of figure 4 are applied. The purged gas stream from the liquefaction unit is recycled to the membrane feed flue gas stream in order to enhance system performance. At the present the membrane separation and the liquefaction are modelled independently and calculations are performed iteratively as the feed flow and CO₂ concentration vary due to the recycle stream. The calculations are converging in just a few iteration steps. The recycle stream contains both CO₂ and N₂, and thus the average CO₂ concentration in the membrane system deviates from equation (3) is evaluated using

$$\bar{x}_{CO_2,f} = \frac{\frac{Q_{CO_2,f,including\ liquefaction\ recycle}}{Q_{f,including\ liquefaction\ recycle}} - x_{CO_2,r}}{\ln\left(\frac{Q_{CO_2,f,including\ liquefaction\ recycle}}{Q_{f,including\ liquefaction\ recycle}} / x_{CO_2,r}\right)} \quad (6)$$

Calculations are made with a permeate pressure of 0.2 bar, CO₂ permeance of $7.5 \cdot 10^{-9}$ m³(STP)/(m²sPa), and as a baseline a liquefaction pressure of 33.5 bar and a membrane separation factor of 40. Figure 8 presents the membrane area per unit flow versus feed pressure for a feed flow containing 20% CO₂. The recycle flow from the liquefaction unit raises this concentration 20.2 – 20.4% for 60% CO₂ recovery and 20.4 – 20.9 % for 80% CO₂ recovery. The CO₂ concentration in the permeate is 60 – 67% for 60% CO₂ recovery and from 46 – 65% for 80% CO₂ recovery. The effect of membrane separation factor is only observed at low pressure ratios of the membrane system, see figure 9. The liquefaction pressure has hardly any effect on the membrane system performance, see figure 10.

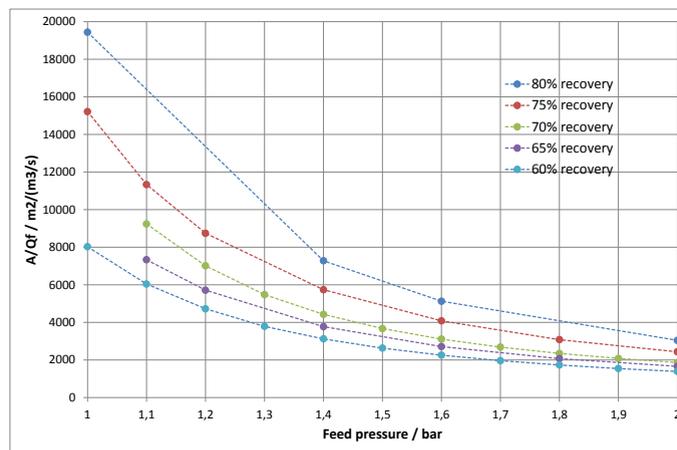


Fig. 8. Membrane area per unit feed flow versus feed pressure at indicated CO₂ recovery at indicated CO₂ recovery. Permeate pressure is 0.2 bar, liquefaction pressure is 33.5 bar, and CO₂ concentration in the feed flow is 20%.

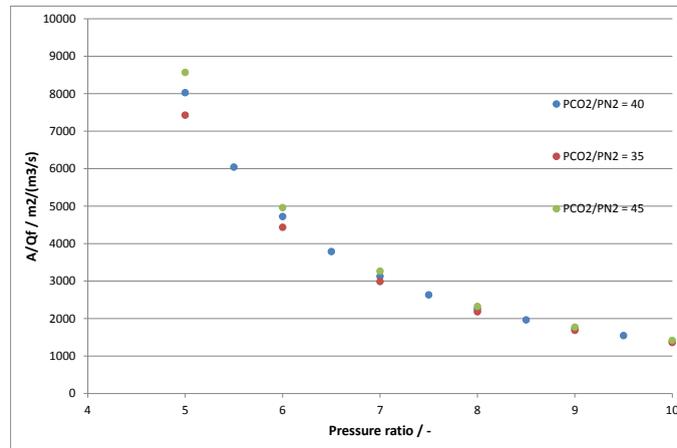


Fig. 9. Membrane area per unit feed flow versus pressure ratio for 3 membrane separation factors. Permeate pressure is 0.2 bar, liquefaction pressure is 33.5 bar, CO₂ concentration in the feed flow is 20% and CO₂ recovery is 60%.

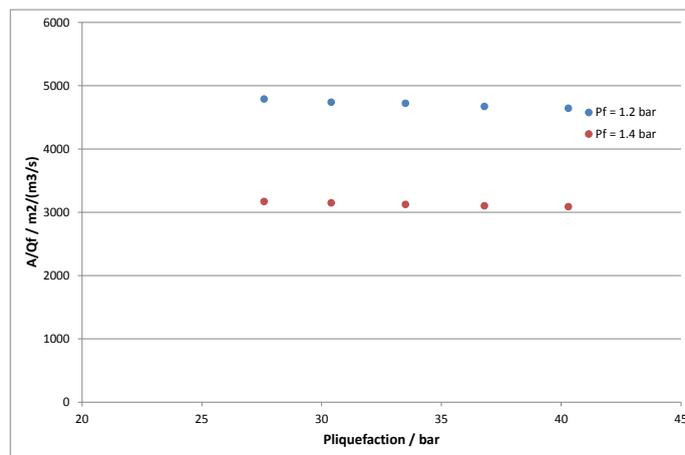


Fig. 10. Membrane area per unit feed flow versus liquefaction pressure. Permeate pressure is 0.2 bar, feed pressure of the membrane system is 1.2 or 1.4 bar, CO₂ concentration in the feed flow is 20% and CO₂ recovery is 60%.

5. Discussion and conclusions

The following conclusions are drawn from the performed calculations.

- The required membrane surface area is a strong function of CO₂ concentration in the flue gas from the cement kiln, desired CO₂ recovery, pressure ratio across the membrane, membrane separation factor and CO₂ permeance.
- The membrane-assisted CO₂ liquefaction with a single membrane unit requires a substantial CO₂ concentration in the cement kiln flue gas, preferably significantly higher than 15%. Substantial recovery of CO₂ can be realized with a CO₂ concentration of 20% and a recycle of the purged waste stream from the liquefaction unit to the inlet of the membrane unit.
- A permeate pressure of 0.2 bar is assumed in calculations. Any improvement in lowering this pressure in the actual process is highly beneficial.

From the technical performance evaluation of the membrane system and the liquefaction unit, one can infer data for an economic evaluation of the CO₂ capture technology, based on process conditions, pumping and cooling requirements and sizing of units. For the economic evaluation, real data is needed regarding CO₂/N₂ separation

factor, and CO₂ permeance of state-of-art and commercially available membranes. The experiments need to account for the eventual plasticizing effect and co-permeation of H₂O, as well as the temperature of the feed gas, as the flue gas may contain 6-10% water and the exhaust temperature is the range of 300-350 °C. Polymeric membranes are not suited for these high temperatures. In [7] it is noted that in a similar CO₂ recovery application, the “membrane is nearly transparent to water vapor, but has relatively small N₂ and O₂ permeance”. The conditioning of the flue gas has not been considered in this study, and the requirements and design of front-end conditioning will depend on actual membrane performance.

Acknowledgements

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