Abstract

The aim of the MEM-BRAIN project is the development and integration of gas separation membranes for zero-emission fossil power plants. This will be achieved by selective membranes with high permeability for CO₂, O₂ or H₂, so that high-purity CO₂ is obtained in a readily condensable form. The project is being implemented by the “MEM-BRAIN” Helmholtz Alliance consisting of research centres, universities and industrial partners.

The MEM-BRAIN project focuses on the development, process engineering, system integration and energy systems analysis of different gas separation membranes for the different CO₂ capture process routes in fossil power plants.

Keywords: zero-emission power plants; gas separation; ceramic membranes; polymeric membranes; process engineering; system integration; energy systems analysis

1. Introduction

The reduction or elimination of CO₂ emissions originating from electricity generation plants fuelled by coal or gas is a major target in the current socio-economic, environmental and political situation involving discussions on how to reduce greenhouse gas emissions such as CO₂. To reduce CO₂-emissions by 50 to 60% up to 2050, as proposed by the EU and other industrial countries, a significant contribution is required on the part of carbon capture and storage (CCS). One way to achieve a reduction is the introduction of gas separation techniques that make use of membrane technology, which is associated with significantly lower efficiency losses compared with conventional separation
technologies. CO₂, O₂ and H₂ separation is achieved by selective membranes with high permeability, so that CO₂ is obtained in a readily condensable form. Although membranes are already being used for material separation in other fields (e.g. the chemical industry), membranes for separating the technically relevant gases in fossil power plants are still far from being suitable for industrial applications. Strategies for novel membranes mean that materials science and technology is at the main focus of research and technology development. Decisive results based on a parallel investigation of (i) design of components and equipment, (ii) integration into power plants and the related process engineering, and (iii) energy systems analysis will pave the way to efficient, low-cost CCS.

As part of the Alliance Programme of the German Helmholtz Association (HGF) a new research project (“MEM- BRAIN” – Gas separation membranes for zero-emission fossil power plants) was started October 2007. The project is meeting a long-term scientific and technological challenge with a time horizon for significant commercialization after 2020. Membrane systems which provide efficient and low-cost technologies for CO₂ separation will become a key technology in power plants in the same way as turbomachinery.

The development of novel membranes for advanced power plant technology requires existing expertise to be focused on the topics of materials and design, nanoscale structures and functional layer systems, construction of complex components and systems as well as on the process engineering design of new power plants.

The Helmholtz Alliance “MEM-BRAIN” consists of 12 research organizations: Forschungszentrum Jülich (FZJ, D), GKSS-Forschungszentrum Geesthacht (GKSS, D), DESY/HASYLAB (D), Helmholtz Zentrum Berlin (HZB, D) and Ernst Ruska Centre (ER-C, D), Hermsdorf Institute of Technical Ceramics (HITK, D), Flemish Institute for Technological Research (VITO, B), Consejo Superior de Investigaciones Científicas (CSIC, E), the universities of Aachen (RWTH, D), Bochum (RUB, D), Karlsruhe (UK, D), Twente (UT, NL). Five industrial partners ensure that the results are applied in an industrial context: EnBW, GMT, Planse SE, Shell, Siemens (D).

2. The Four Research Topics of MEM-BRAIN

There are three groups of CO₂ capture concepts with corresponding gas separation tasks, namely

- post-combustion (CO₂/N₂ separation)
- pre-combustion (H₂/CO₂ separation) and
- oxyfuel combustion (O₂/N₂ separation).

Different kinds of membranes are considered for each concept:

- Microporous ceramic membranes operating at temperatures of up to 400°C can be used for pre-combustion and possibly for post-combustion sequestration.
- Polymeric membranes working at temperatures of up to 200°C are candidates for pre-combustion and in particular post-combustion processes.
- Dense ceramic membranes are necessary for oxyfuel processes working at 800-1000°C (mixed ionic-electronic conductors, MIEC) and are possible candidates for pre-combustion operation at approx. 600°C (proton conductors).
The principle advantage of the MEM-BRAIN project is the parallel, networked (iterative) development of the membrane and the power plant technology areas in an energy system. To tackle the described challenge the work of the Alliance has been structured into four Research Topics (Fig. 1).

The technical basis is provided by two of the Research Topics in the field of materials science, one developing ceramic membranes (RT 1), the other polymeric membranes (RT 2). Main scientific challenge is the development of membrane systems with high permeability, specific selectivity and long-term stability. In application these systems have to be included into power plants and an energy system which define additional boundary conditions. Close cooperation with systems analysis groups is necessary to identify optimum operation conditions with minimized efficiency losses and environmental impacts. Two Research Topics consider the integration of capture techniques into the power plant and the energy supply system as a whole (RT 3, 4).

2.1. Research Topic 1: High- and intermediate-temperature ceramic membranes

Research Topic 1 (RT 1) is concerned with material synthesis and processing as well as the characterization and modelling of ceramic membranes. The overall aim of RT 1 is the identification of and concern with fundamental issues and further development of the most promising ceramic membranes for the separation of H$_2$/CO$_2$, O$_2$/N$_2$ and possibly CO$_2$/N$_2$ and others. RT 1 will provide the information necessary to enable the most promising membrane options to be selected for integration into power plant process scenarios aimed at CO$_2$ capture. Important research goals to be addressed include:

- Development and characterization of ceramic molecular sieving membranes, including zeolite and sol-gel-derived membranes, for H$_2$/CO$_2$ separation.
- Development and characterization of dense ceramic proton-conducting and mixed proton-/electron-conducting membranes for H$_2$/CO$_2$ separation.
- Development and characterization of dense ceramic mixed oxygen ionic-electronic conducting membranes for O$_2$/N$_2$ separation.
- Modelling of transport issues and surface exchange behaviour (especially for dense ceramic membranes).
- Design and development of a demonstration unit (Proof-of-concept) for O$_2$/N$_2$ separation.

2.2. Research Topic 2: Polymeric and hybrid membranes for temperatures up to 200°C

Research Topic 2 (RT 2) is concerned with material synthesis (new polymers, fixed carriers and organic-inorganic hybrids), membrane manufacture and characterization as well as module development on a pilot scale for separation in temperature ranges of up to 200°C. The main objective of RT 2 is the development of polymeric and organic/inorganic hybrid membranes for CO$_2$/N$_2$ separation. Membranes should be available which exhibit a carbon dioxide flux of more than 1 m$^3$/m$^2$ h bar and a CO$_2$/N$_2$ selectivity of more than 60. At the end of the project, data will be available for ranking materials and designs for each power plant concept. Membranes with a CO$_2$/N$_2$ selectivity of more than 100 are envisaged. These membranes will be produced on pilot scale (100 m$^2$ or more). Technical membrane modules will be produced with a membrane area of at least 10m$^2$ each.

2.3. Research Topic 3: Process engineering and system integration

In Research Topic 3 (RT 3) all the power plant processes are modelled and the required technical parameters or acceptable ranges for future membranes are derived. These are selectivity and permeability as well as boundary conditions such as mechanical, thermal and chemical loads. The power plant process chain has to be modified to accommodate the performance of the developed membranes. This leads to an iterative approach to achieve a compromise between requirements and performance.
The partners in RT 3 investigate and compare the different process routes and their potential for using membranes for CO₂ capture. The major aim of RT 3 is to link membrane development with the reality of power plant processes. Based on this central role the following major goals can be defined for RT 3:

- To provide RT 1 and RT 2 with the proper boundary conditions that membranes have to face and withstand in terms of temperature, pressure and gas composition. Also, to define testing procedures in cooperation with RT 1 and RT 2 for the evaluation of membrane materials and membranes with respect to performance and stability under power plant conditions.
- To define the optimal power plant process for the membranes developed and delivered by RT 1 and RT 2, taking into account the membrane limitations in terms of selectivity, permeation rates and thermal and chemical stability.
- To define a limited set of evaluation criteria permitting a quantification of the optimum power plant process parameters.
- To provide a reliable and consistent set of technical process data for the membrane power plant concepts under consideration, their competing CO₂ removal technologies and current power plants based on harmonized assumptions for the major input data, boundary conditions and component performance using state-of-the-art process simulation tools.
- To highlight, quantify and evaluate the differences between membrane power plants compared to competing CO₂ removal technologies and current power plants in terms of technical performance, required hardware modifications or extensions, complexity of plant design.

2.4. Research Topic 4: Energy systems analysis

Research Topic 4 (RT 4) is concerned with an energy systems analysis resulting in an assessment of specific technical, economic and environmental aspects of CO₂ capture as a component of the whole CCS process chain. Therefore information about material composition and the production of the selected membranes from RT 1 and RT 2 is required for life cycle assessments or for evaluating natural resource demands. Results from RT 3 regarding the entire power production cycle allow a comparison to be made with competing CCS technologies. Energy systems analysis provides benchmarks concerning costs compared to other CO₂ avoidance strategies, capacity increase and window of opportunity.

The work is performed as an accompanying energy systems analysis during the research phase for membrane technology. Because the membranes will be used as an important component of future (near-) zero emission power plants as part of a climate protection strategy the analysis will take into account the broader process chain and significant techno-economic aspects of the general energy system. In particular, the aims are

- To characterize ranges of techno-economic requirements for capture technology from subsequent processes, e.g. purity of CO₂ for transport and storage, economies of scale and reliability with respect to CO₂ flows;
- To quantify and assess the impacts on the environment and natural resources, e.g. inventories for relevant inputs and outputs of the process chains for capture, weak point analysis, environmental impact analysis;
- To develop scenarios for the potential of membrane-based CO₂ capture in the energy system, e.g. membrane-based capture technology as part of a climate protection strategy, competing technologies.

3. Results

After the first year preliminary results could be gathered and are used as basis for further investigations.

3.1. Research Topic 1: High- and intermediate-temperature ceramic membranes

3.1.1. Sol-gel-derived membranes

Before the start of the project, first attempts were made to prepare gas-selective TiO₂/ZrO₂ layers on conventional substrates commonly used for silica membranes but so far without selectivity. Moreover, the mesoporous γ-Al₂O₃ is expected to have limitations with respect to hydrothermal stability and will be replaced by a mesoporous layer with higher stability. Indications were found that TiO₂/ZrO₂ membranes are densified under hydrothermal conditions. Therefore one other material, Ta₂O₅, will be included in the working plan.
The following results were achieved:
- First stability tests of different TiO$_2$/ZrO$_2$ compositions indicated a higher stability for ZrO$_2$-rich compositions. Therefore membrane preparation will focus on this direction. Stability tests will be continued.
- The quality of mesoporous ZrO$_2$ layers was improved significantly. Thin defect-free ZrO$_2$ layers were successfully prepared on top of this intermediate layer (Fig. 2).
- The sol-gel chemistry of Ta$_2$O$_5$ starting from tantalum ethoxide Ta(C$_2$H$_5$O)$_5$ was investigated. Stable sols with nanosized particles were prepared by hydrolysis and condensation at room temperature, and storage at -28 °C. The sols were used to prepare both unsupported and supported membranes. The membranes display Knudsen behaviour in gas separation measurements of He, H$_2$, N$_2$, CH$_4$ and SF$_6$. Further optimization of sol-gel recipes and/or coating procedures is required in order to develop membranes with molecular sieving properties.

3.1.2. Zeolite membranes

Three types of zeolites, hydroxo sodalite (H-SOD, S-SOD), NaA-type zeolite and ITQ-29 were selected as membrane materials for the project. H-SOD is a 6-ring zeolite.

The following results were achieved:
- H-SOD and ITQ-29 were prepared as pure crystalline powders
- Powders of NaA (commercial), H-SOD and S-SOD were tested for thermal and hydrothermal stability. All materials are stable at 400°C in a dry atmosphere and in 2.5 vol% water, no material was stable at 270°C or in saturated water steam (57 bar), S-SOD was most stable (800°C, 2.5Vol% H$_2$O and 180°C, 10 bar water steam)
- Flat support discs were seeded by slip coating with zeolite slurries prepared from the powders (NaA, H-SOD, S-SOD). After hydrothermal crystallization (intergrowing of seed crystals to form a dense zeolite layer) the substrates were completely covered by zeolite layers (SEM) (Fig. 3).
3.1.3. Mixed ionic-electronic conductors (MIEC)

Three promising materials were selected for further investigation, including the perovskite oxides $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF5582) and $\text{BaCo}_x\text{Fe}_{1-x}\text{Zr}_2\text{O}_4$ (BCFZ) for the oxyfuel process without sweep gas, and doped ceria, $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ (CGO), for the pre-combustion process. The oxyfuel process with flue gas as sweep was not taken into consideration. Up to now, none of the known materials (perovskites, $\text{La}_2\text{NiO}_4$) are stable under these harsh conditions (CO$_2$, SO$_2$, ash etc.).

A first small comparative oxygen permeation study performed in cooperation between some of the project partners has shown that permeation flux measurements are sensitive to the geometrical and flow conditions of the respective experimental set-up.

BSCF5582 was investigated comprehensively concerning its crystal structure, (Fig. 4) thermo-chemical and thermo-mechanical properties in order to correlate these and find optimum working conditions in close cooperation with RT 3, e.g. temperature, atmospheres. For instance, increasing temperature leads to both increasing permeation rates and creep rates.

BCFZ was investigated in order to compare its functional properties and stability with BSCF5582. This includes powder synthesis, sample processing and selective characterization. Moreover, a defect and transport model was developed.

Doped ceria is expected to be more stable than perovskites, particularly BSCF5582, in reducing atmospheres and to achieve sufficient oxygen permeation in an air/methane gradient (pre-combustion) when produced as a thin film (<100 μm thickness). The first $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2.8}$ ultrathin layers were fabricated on a NiO/ZrO$_2$ porous support.

![HTEM of perovskite](image)

3.1.4. Ceramic proton-conducting membranes

This work package aims to develop and optimize new proton-conducting materials and membranes by enhancing the electronic and protonic conduction, stability with respect to wet CO$_2$, thermo-mechanical properties and manufacturing issues. This integrated research focuses on a new class of crystalline oxide-based conductors, i.e. the system $\text{Ln}_{2-x}\text{Ca}_x\text{WO}_4$, which presents significant protonic and electronic conductivity at intermediate temperatures. The activities include a parallel study of (i) fundamental properties aiming at understanding and designing new materials and (ii) application-oriented properties to ensure their fast and reliable manufacture and operation.

3.2. Research Topic 2: Polymeric and hybrid membranes for temperatures up to 200°C

3.2.1. Pebax-based membranes

It is well known that ethylene oxide units have an affinity to carbon dioxide. Homopolyethylene oxide consists of EO monomeric units, but its disadvantage is its strong tendency to crystallize and consequently its gas permeability is low. Block copolymers containing EO units as poly(amide-b-ether) have been identified as alternative materials for this purpose. Polymers of this kind are produced by Arkema under the trade name Pebax. Pebax is available in many different grades. For this project the very hydrophilic grade MH 1657 was selected. This grade contains 60wt.% PEO and 40 wt.% nylon 6. In order to increase the carbon dioxide permeability of Pebax, blends with liquid polyethylene glycol (PEG200) were prepared. It was demonstrated that Pebax 1657 is very compatible with PEG200. Blends of Pebax with up to 50wt.% PEG200 were prepared, and had excellent mechanical properties. The carbon dioxide permeability was more than doubled by the addition of 50wt.% PEG200 (from 73 to 151 barrer). The CO$_2$/H$_2$ selectivity was enhanced from 9 to almost 11. These results were correlated with morphological and structural changes in the copolymer system. Higher PEG content led to lower crystallinity in the membranes and
high interaction between EO unit and carbon dioxide. Consequently, diffusivity and permeability showed a jump after 20 wt% of PEG. During the first months of the project, it was demonstrated that a Pebax/PEG blend showed a superior performance for carbon dioxide capture compared to pristine Pebax.

3.2.2. PolyActive-based membranes
Besides Pebax another multi-block copolymer selected for membrane development was a copolymer consisting of poly(ethylene oxide)-poly(butylene terephthalate) known under the trade name PolyActive (IsoTisOrthoBiologics, USA).

Different PEO-PBT multi-block copolymers were used to prepare carbon dioxide selective membranes. The influence of PEO block length and weight fraction was studied. The CO₂ permeability runs through a maximum when plotted versus the molecular weight of the PEO block (constant weight fraction of PEO block). According to the estimated values (tailor-made polymer), a molecular weight of 2000 or 2500 g/mol of PEO in the PEO-PBT multi-block copolymer represents the highest CO₂ permeability.

3.3. Research Topic 3: Process engineering and system integration

3.3.1. Reference power plants
For a conventional combustion plant the reference power plant NRW (RKW-NRW) was chosen. A process model was set up in AspenPlus. The model includes the flue gas side with combustion chamber, boiler and flue gas cleaning, and the water steam cycle with boiler, turbines and preheating section. The thermal power input is defined as 1210 MW and cases with hard coal (HC) and dried lignite (LC) were simulated. The simulated net efficiencies of 45.9 % (HC) and 44.5 % (LC) provide a good match to the values given in the literature.

The IGCC in Puertollano was chosen as a conventional gasification plant. The objective of integrated gasification combined cycle (IGCC) processes is to exploit the high efficiencies of natural-gas-fired combined cycle power plants with coal or other carbon-rich solid fuels like biomass or waste. The net efficiency of the simulations is in relation to each other: $\eta_{\text{LHV,MEM-BRAIN}} = 50.31$ % and $\eta_{\text{LHV,Kloster}} = 50.5$ % (excluding the auxiliary power consumption of the ASU).

3.3.2. Post-combustion capture
As a conventional separation method only the MEA (monoethanolamine) scrubbing technology is a realistic candidate today for capturing CO₂ from existing coal-fired steam power plants (SPP). On the other hand, from the different routes of membrane power plants, only the CO₂/N₂ separating membrane can be applied to all existing steam power plants. Therefore, MEA scrubbing is the direct competitor of the CO₂ membrane concepts which have to be developed, simulated and optimized in MEM-BRAIN.

Based on a study of the literature, a typical MEA wash process is defined and calculated, which is characterized by 90% CO₂ separation degree and a CO₂ purity approaching 99 mol%.

The efficiency loss for CO₂ compression/liquefaction amounts typically to 3-4 % points, which corresponds to an electric energy demand of about 100 kWh/t CO₂ (separated). The electric energy loss for capture is much higher:

<table>
<thead>
<tr>
<th>Process</th>
<th>Electric Energy Demand</th>
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<tbody>
<tr>
<td>Capture</td>
<td>210 kWh/t CO₂</td>
</tr>
<tr>
<td>(efficiency loss 6-7 % points)</td>
<td></td>
</tr>
<tr>
<td>Compression</td>
<td>100 kWh/t CO₂</td>
</tr>
<tr>
<td>(efficiency loss 3-4 % points)</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>310 kWh/t CO₂</td>
</tr>
<tr>
<td>(total efficiency loss about 10 % points)</td>
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From detailed energetic simulations carried out for a single membrane (CO₂/N₂ selectivity 40:1) and orienting simulations for two connected membranes (completely cascaded), the permeate vacuum concepts (about 50 mbar) seem to be energetically more promising than the feed compression/expansion concepts (about 5 bar). Taking into account the fact that in future the handling and storage of pure as well as impure CO₂ (<90 mol%, resulting in a demand for greater storage volume) may exist in parallel, three strategy routes will be investigated in MEM-BRAIN, leading to the following expected total specific energy demand (for compression/liquefaction a constant energy demand of 100 kWh/t CO₂ is assumed):

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Electric Energy Demand</th>
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<tbody>
<tr>
<td>Single membrane:</td>
<td>210 kWh/t CO₂</td>
</tr>
<tr>
<td>(CO₂ purity 80 mol%)</td>
<td></td>
</tr>
<tr>
<td>Partly cascaded membranes:</td>
<td>~250 kWh/t CO₂</td>
</tr>
<tr>
<td>(CO₂ purity ~90 mol%)</td>
<td></td>
</tr>
<tr>
<td>Two-cascaded membranes:</td>
<td>~300 kWh/t CO₂</td>
</tr>
<tr>
<td>(CO₂ purity ~95 mol%)</td>
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3.3.3. Pre-combustion capture
The literature study revealed that the most widely proven methods for carbon capture in IGCC power plants are physical absorption processes like RECTISOL and SELEXOL. The literature study also revealed that there is a huge data spread, which shows differences in efficiency losses from 5 to 11%.
However, with regard to the chronology of the publications, it is obvious that there is a trend towards higher efficiency losses. This could be due to an overoptimistic interpretation of the results in the early research phases.

3.3.4. Oxyfuel combustion
A literature study in the field of oxyfuel power plant processes was carried out. Differences to conventional power plants were detected with respect to auxiliary energy demand, false air and recirculation. The efficiency drop compared to air-fired power plants is about $\Delta\eta = 8 - 11\ %$-points mainly due to the energy required for air separation and compression of CO$_2$. The energy demands of both processes depend to a large extent on the oxygen purity and have an opposite effect on each other.

3.4. Research Topic 4: Energy systems analysis

3.4.1. Characterization of specific technical and economic aspects concerning CO$_2$ transport and storage
The main restrictions to impurities are caused by the subsequent processes of compression, transport and storage. Technical, chemical or physical effects of various impurities for compression, transport, storage and health security were investigated. The multicomponent contaminations have a major impact on the compression energy being more negatively affected by contaminants with a low molar mass than with a high one. Contaminations might also lead to an unwanted phase change depending on the kind of contamination or temperature and pressure. With respect to transport, this phase change can yield an increasing volume and therefore lead to increasing energy demand for pumping the gas stream through the pipeline and a high corrosion potential. Impurities can also decrease the level of utilization of the storage capacity and might change the storage geology. For a typical storage condition (100bar and 40°C) only half as much flue gas from a pre-combustion plant can be stored compared to pure CO$_2$, for an oxyfuel gas it is about 30% less.

3.4.2. Screening LCA for membranes and power plants and resource balances
In the first phase main effort was put in the modelling and analyses of power production with carbon capture using non-membrane technology. For each process route a currently most promising competing technology was defined. The results obtained in the process simulation were transformed into life cycle data. The process data were combined and completed by data considering upstream and downstream processes, such as coal supply or waste water treatment and the potential impacts connected with the production of 1 kWh$_e$ are assessed. Typical impact categories beside global warming potential are acidification, eutrophication, ozone depletion potential, human toxicity but also resource use.

3.4.3. Energy systems model analysis
CCS represents one measure amongst many other mitigation options. Therefore, the application of membranes for capture competes not only against other capture technologies but CCS itself competes with other measures. One possibility of determining optimum-cost mitigation strategies is the application of bottom-up energy system models. By means of the IKARUS optimization model, scenarios have been generated that permit CCS to be classified within the framework of a national mitigation strategy for Germany. Within the framework of these calculations, reduction scenarios will be defined using penalty prices for CO$_2$ emissions resulting in reduced CO$_2$ emissions and different mitigation measures.

4. Acknowledgements

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