Final Draft
of the original manuscript:

Czyperek, M.; Zapp, P.; Bouwmeester, H.J.M.; Modigell, M.; Ebert, K.; Voigt, I.; Meulenberg, W.A.; Singheiser, L.; Stoever, D.**:**

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In: Journal of Membrane Science (2010) Elsevier

DOI: 10.1016/j.memsci.2010.04.012

Gas separation membranes for zero-emission fossil power plants: MEM-BRAIN

M. Czyperek[a]*, P. Zapp[a], H. J. M. Bouwmeester[b], M. Modigell[c], K. Ebert[d], I. Voigt[e], W. A. Meulenberg[a], L. Singheiser[a], D. Stöver[a]

[a]Forschungszentrum Jülich GmbH, Institute of Energy Research, Leo-Brandt-Str. 1, D-52425 Jülich, Germany
[b]University of Twente, Department of. Science and Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands
[c]RWTH Aachen University, Department of Chemical Engineering, Turmstr. 46, D-52056 Aachen, Germany
[d]GKSS-Forschungszentrum Geesthacht GmbH, Institute of Materials Research, Max-Planck-Str. 1, D-21502 Geesthacht, Germany
[e]Hermsdorfer Institut für Technische Keramik e.V., Michael-Faraday-Str. 1, D-07629 Hermsdorf/Thuringia, Germany

Abstract

The objective of the "MEM-BRAIN" project is the development and integration of ceramic and polymeric gas separation membranes for zero-emission fossil power plants. This will be achieved by membranes with high permeability and selectivity for either CO_2, O_2 or H_2, for the three CO_2 capture process routes in power plants, enabling capturing of CO_2 with high-purity in a readily condensable form.
For the pre-combustion process, ceramic microporous membranes operating at intermediate temperatures (≤ 400°C) are developed for H_2/CO_2 separation. For the oxyfuel process, dense ceramic mixed oxygen ionic-electronic conducting membranes operating at 800-1000°C are developed for O_2/N_2 separation. The perovskite-type oxide $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) is taken as the reference material for this application. For the post combustion process, polymeric and organic/inorganic hybrid membranes are developed for the CO_2/N_2 separation at temperature up to 200°C. New hybrid organic/inorganic membranes with inorganic molecular sieves will be prepared, characterized and incorporated in polymer matrices.
Additional to the development of membranes the integration of the membranes into power plants by modelling and optimization is considered. Finally, specific technical, economic and environmental properties of CO_2 capture as a component of a CCS process chain are assessed, analysing at the energy supply system as a whole.
Keywords: zero-emission power plants; gas separation; ceramic membrane; polymeric membrane; process engineering; system integration; energy systems analysis

1. Introduction

CO_2 is one of the greenhouse gases that contributes significantly to the global climate warming. Therefore, the reduction or elimination of CO_2 emissions from electricity generation power plants fuelled by coal or gas is a major target in the current socio-economic, environmental and political discussion. Scenarios about the future global energy requirements forecast an increasing demand for electricity, with 44 % using coal as fuel in 2030 [[1]. Today, power plants contribute more than 40 % of the worldwide anthropogenic CO_2 emissions; they are by far the biggest point sources of CO_2-production and are therefore the main focus of CO_2 capture and storage technologies (CCS). Current energy scenarios of the International Energy Agency (IEA) show an increasing importance of CCS technology within global CO_2 mitigation strategies [[2]. Since several years the development, improvement and adaptation of CCS technologies have received considerable attention [3]. The technical maturity of specific CCS components varies greatly. Some technologies are extensively deployed in mature markets, primarily in the oil and gas industry. For electricity production most CCS components are still in the research, development or demonstration phases. Mayor challenges are a sizable reduction in efficiency connected with an increase in power generation costs. Capture technologies using solvents additionaly face environmental problems due to degradation. No experience with capture facilities at power plant scale exists but they are expected to be huge plants in themselves.
One option to overcome all this challenges is the development and improvement of membranes for gas separation. However, there are several technical hurdles which have to be solved first [4], [5]. The key scientific and

* M. Czyperek. Tel.: +49-2461-61-5450; fax: +49-2461-61-2455.
E-mail address: m.czyperek@fz-juelich.de

technological challenge for membrane systems are high permeability, specific selectivity and long-term stability up to 100,000 hours. The use of membrane technology is expected to have with significantly lower efficiency losses compared to conventional separation technologies. Membranes that are already being used for material gas separation in other fields (e.g. the chemical industry), are still far from being suitable for industrial applications. Strategies for novel membranes bring materials science and technology into the main focus of research and technology development, such as functional layers and porous structures in the nanometre range, as well as the development of mixed-conducting oxides by means of theoretical materials design approaches and design of components under operating conditions based on their physico-chemical and mechanical properties. The optimized integration of membrane systems into power plants as well as the analysis of the entire system encourages these efforts.

To address this mission the integrated "MEM-BRAIN" was started fall 2007 as part of the Alliance Programme of the German Helmholtz Association (HGF). The principle advantage of the project is the parallel, networked (iterative) development of the membrane materials by (i) design of components and equipment, (ii) integration into power plants and the related process engineering, and (iii) energy systems analysis.

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 Investigationes Cientificas (CSIC, E), the universities of Aachen (RWTH, D), Bochum (RUB, D), Karlsruhe (KIT, D), Twente (UT, NL). Five industrial partners ensure that the results are applied in an industrial context : EnBW (D), GMT (D), Plansee SE (A), Shell (NL), Siemens (D). The project is meeting a long-term scientific and technological challenge with a time horizon for significant commercialization after 2020.

2. The Four Research Topics of MEM-BRAIN

There are three groups of CO_2 capture concepts with corresponding gas separation tasks, namely

- post-combustion (CO_2/N_2 separation)
- pre-combustion (H_2/CO_2 separation) and
- oxyfuel combustion (O_2/N_2 separation) (**Figure 1**).

Fig. 1: The three CO_2 capture concepts

Different kinds of membranes are considered for each concept:

- Polymeric membranes working at temperatures of up to 200°C are candidates for pre-combustion and in particular post-combustion processes.
- Microporous ceramic membranes operating at temperatures of up to 400°C can be used for pre-combustion and possibly for post-combustion capture.
- 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 temperatures above 600°C (mixed proton-electronic conductors).

To face the described challenges the work of the Alliance has been structured into four Research Topics. 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 and manufacture of novel membrane systems with high permeability, specific selectivity and long-term stability under application conditions. These systems have to be included into power plants and an energy system which define additional boundary conditions. It has to be proved that membrane systems have less energy losses as competing capture technologies with comparable costs. Membrane area has to be kept small. Close co-operation with systems analysis groups is necessary to identify optimum operation conditions with low 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 characterization and modelling of the performance of ceramic membranes. The overall aim is the identification and further development of the promising candidate membrane materials 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 selection of the most promising options for integration of membranes 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

Research Topic 2 (RT 2) is concerned with material synthesis, membrane manufacture and characterization as well as module development on a pilot scale for separation in temperature ranges of up to 200°C. Polymeric membranes are the furthest developed ones.
Polymeric and organic/inorganic hybrid membranes are being developed for CO_2/N_2-separation (post combustion process) as well as for CO_2/H_2-separation (precombustion process). In contrast to the membranes developed in RT 1, these membranes are more permeable for CO_2 than for H_2. Besides pure polymeric membranes, new hybrid organic/inorganic membranes with inorganic molecular sieves will be prepared. 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 10 m^2 each.

2.3. Research Topic 3: Process engineering and system integration

The major aim of Research Topic 3 (RT 3) is to link membrane development with the reality of power plant processes. Therefore, the different power plant process routes are modelled and their potential of using membranes for CO_2 capture are analysed. The required technical parameters are selectivity and permeability as well as boundary conditions such as mechanical, thermal and chemical loads. They form the basis for process simulation to evaluate the performance due to the different CO_2 removal technologies.
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.
Based on this central role the following major goals can be defined:

- To provide 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 the membrane developers 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, 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 CO_2 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 CO_2 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) even widens the frame by performing an accompanying energy systems analysis during the research phase for membrane technology. It is concerned with an assessment of specific technical, economic and environmental aspects of CO_2 capture as a component of the whole CCS process chain including also CO_2 transport and storage. For life cycle assessments or for evaluating natural resource demands information about material composition and the production of the selected membranes from the membrane developers (RT 1, 2) is required. Results from plant modelling (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 CO_2 avoidance strategies, capacity increase and window of opportunity. The aims are:

- Characterization of ranges of techno-economic requirements for capture technology from subsequent processes, e.g. purity of CO_2 for compression, transport and storage;
- Quantification and assessment of 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;
- Description of the potential of carbon capture in the conversion sector as part of a German climate mitigation strategy.

3. Results

In all research areas 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 TiO_2/ZrO_2 layers on conventional substrates commonly used for silica membranes but so far without selectivity. Moreover, the mesoporous γ-Al_2O_3 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 TiO_2/ZrO_2 membranes are densified under hydrothermal conditions. Therefore one other material, Ta_2O_5, 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 (**Figure 2**).
- The sol-gel chemistry of Ta_2O_5 starting from tantalum ethoxide $Ta(C_2H_5O)_5$ 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.

Fig. 2: Microporous ZrO_2 membrane on top layer of a high quality mesoporous ZrO_2 layer

3.1.2. Zeolite membranes

Three types of zeolites, sodalite (SOD), NaA-type zeolite and ITQ-29 were selected as membrane materials for the project. SOD is a 6-ring zeolite. The pore size of only 2.5 Å should allow the high selective H2-separation from gas mixtures by size exclusion. NaA and ITQ-29 are 8-ring zeolites with a pore size of 4 Å. The larger pores are giving a lower selectivity but higher permeances through the membrane. ITQ-29 is a pure silica zeolite with a potential high hydrothermal stability.

The following results were achieved:

- SOD and ITQ-29 were prepared as pure crystalline powders
- Powders of NaA (commercial), SOD and ITQ-29 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 in saturated water steam (57 bar), SOD was most stable (800°C, 2.5Vol% H_2O and 180°C, 10 bar water steam)
- Flat support discs were seeded by slip coating with zeolite slurries prepared from the powders (NaA, SOD,). After hydrothermal crystallization (intergrowing of seed crystals to form a dense zeolite layer) the substrates were completely covered by zeolite layers (SEM) (**Figure 3**).
- Two types of membranes (SOD, NaA) were tested for single gas permeances. A H_2/SF_6 permselectivity of 7.7 and a H_2 permeance of 2,300 l/(m²·h·bar) indicated gas permeation through non-zeolite pores of the NaA membrane. Low permeances of 2 l/(m²·h·bar) (SF6) - 18 l/(m²·h·bar) (H_2) were measured with SOD membranes giving evidence of a well intergrown but nearly impermeable membrane. The blocking of zeolite pores with water was assumed to be the reason for the low permeances. Therefore one membrane was dried at 250°C. Increased permeance by the factor of 1,000 was the result. Higher fluxes (32,000 l/(m²·h·bar) H_2) were measured for a two times synthesised SOD membrane. But in all cases no mole sieving separation behaviour was found up to now. Drying as well as double syntheses cracked the membranes.

Fig. 3: SOD membrane layer on top of an α-Al_2O_3 support disc

3.1.3. Mixed ionic-electronic conductors (MIEC)

Up to now three major candidate materials were selected for further in-depth investigations, including the perovskite oxides $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) and $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ) and the fluorite-structured oxide $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CGO). Both BSCF5582 and BSCFZ are investigated for potential application in the oxyfuel process without sweep gas. CGO is investigated for potential use in the pre-combustion process. Oxyfuel combustion with flue gas recycle is not taken into consideration since none of the presently known membrane materials with appreciable oxygen fluxes are found to be stable under the harsh conditions (CO_2, SO_2, ash etc.) as encountered in oxyfuel combustion.

A round-robin study was performed towards the oxygen flux exhibited by BSCF5582. The measurements showed that the results are sensitive to the geometrical and flow conditions of the experimental set-ups used in the different laboratories of the partners involved in the MEM-BRAIN project. BSCF5582 was further investigated comprehensively concerning its crystal structure, structural stability in different gas phase environments, which includes its stability against the presence of CO_2 contaminants in the gas phase, oxygen surface exchange, and thermo-chemical and -mechanical properties. Typical results of HR-TEM imaging of BSCF5582 are shown in Fig. 4. BSCF5582, however, shows limited structural stability as a slow structural transformation occurs from cubic to hexagonal upon cooling below ~800°C [6].The composition BSCF5582 is therefore mainly regarded as a reference material. Similar studies towards compositions derived from parent BSCF5582, in which it is attempted to stabilize its cubic structure by partial substitution with redox-stable dopant ions, are currently underway. Among a number of other compositions, major research is conducted towards BCFZ. This composition was earlier proposed by Tong et. al. [7] for use in partial oxidation of methane. Doped ceria as considered for possible application in the pre-combustion route is known to be far more stable than the afore-mentioned perovskite compositions, especially in reducing atmospheres. Measurements have demonstrated that viable oxygen fluxes can be achieved by sweeping

CGO membranes with methane, Presently, thin membranes (< 60μm) of CGO are fabricated on NiO/ZrO_2 porous support layers to further optimize the oxygen fluxes.

Fig. 4: HR-TEM of perovskite BSF5582

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, [8], [9], i.e. the system $Ln_{6-x}Ca_xWO_{12}$, which presents simultaneously significant protonic and electronic conductivity at intermediate temperatures (see Figure). The activities include a parallel study of (a) fundamental properties aiming at understanding and designing new materials and (b) application-oriented properties to ensure their fast and reliable manufacture and operation.

The stability under CO_2/H_2O-rich reducing environments at different temperatures (350, 700 and 800 ºC) has been proven [10] for a set of materials, i.e. Ln_6WO_{12} with Ln = {La; Nd; Eu; Er} annealed at different temperatures (900, 1150 and 1350 ºC). The current material development approach applies co-doping strategies, different synthetic routes (sol-gel, solid state reaction and freeze-drying) and fine-tuning of the Ln/W ratio, which influences the final conduction properties as well as the ordering of cations and anions in the lattice and hence originates changes in the cubic fluorite space group and the fluorite symmetry. Nevertheless, it is necessary to manufacture asymmetric supported membranes based on $Ln_{6-x}Ca_xWO_{12}$ materials in order to achieve hydrogen fluxes above 1 $ml{\cdot}min^{-1}{\cdot}cm^{-2}$ at temperatures in the range 800-900 ºC.

Fig. 5: Scheme of the permeation process in a mixed protonic-electronic conducting membrane made of La_6WO_{12}

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

3.2.1. Membrane development with multi-block copolymers

Thin film composite membranes with thins selective separation layers based on multi-block copolymers were developed. The two commercially available polymers are poly(amide-b-ethylene oxide) (Pebax® from Arkema) and poly(ethylene oxide)-poly(butylene terephthalate) (Polyactive® from IsoTisOrthoBiologics, USA). The formulaes of the polymers are given in **Figure 6**. Both polymers possess ethylene oxide segments in the chain which are known to have a high affinity for CO_2 thereby favouring the separation of CO_2 over other gases [11].

The properties of these multi-block copolymers strongly depend on the microstucture as a result of the type of blocks, the composition of each block, the molecular weight and the processing conditions [12].

Fig. 6: Structural formulaes of Pebax® and Polyactive®

The permeability of Pebax® 1657, which was found to be the most promising Pebax with respect to CO_2 separation, strongly depends on the crystallinity caused by the crystallization of the ethylene oxide chains. In the previous phase of the project composites were developed consisting of Pebax® 1657 and different low molecular weight PEG's, either pristine or functionalized. It was shown that by blending Pebax 1657 with the PEG's the crystallinity could be suppressed significantly [13], [14], [15]. At a concentration of 20 wt% of PEG in the blend a sharp increase in diffusivity and consequently, in permeability was observed. Blends of Pebax with 50 wt% of PEG200 showed a CO_2 permeability of 151 Barrer which is twice the permeability of pristine Pebax by maintaining the CO_2/N_2 selectivity.

By adding PEG terminated with different ethers, as for instance dimethylether (DME), it was found that both the CO_2 permeability and the CO_2/H_2 selectivity increased simultaneously [16]. This effect again could be attributed to the change in microstructure, but additionally it was discussed that the presence of the ether groups prevents the formation of hydrogen bonds thereby favouring the transport of CO_2 over hydrogen.

Different Polyactive types were characterized in order to identify the most suitable composition of blocks in the polymer. It was found that for constant content of PEO-blocks the CO_2 permeability strongly depends on the molecular weight of the PEO-unit [17]. The highest CO_2 permeabilities were found for the multi-block copolymers with a molecular weight of the PEO-units between 2000 to 2500 g/mol.
The addition of PEG terminated with different ethers again resulted in an increase in CO_2 permeability [18]. With the addition of 40 wt% PEG terminated with dibutylether an increase of CO_2 permeability from 150 Barrer for the pristine Polyactive to 750 Barrer for the blend could be achieved. This increase in permeability was mainly attributed to the ethylene oxide and total free volume increase in the polymer matrix.

All membranes were manufactured on technical casting and coating machines in the m^2 size. Microporous polyacrylonitrile membranes developed at GKSS were used as supports. The membranes were characterized by single and mixed gas measurements. CO_2/H_2 mixtures of 50/50 vol/vol and 25/75 vol/vol, respectively. With Pebax/PEG membranes mixed CO_2/H_2-selectivities around 9 and were obtained, for CO_2/N_2 the mixed gas selectivity dropped from 75 to around 60, when the pressure increased from 3 to 20 bar [15].

The optimization of the coating technology allowed the production of membranes composite membranes with Pebax/PEG-dimethyl ether layers showing high CO_2 fluxes of >1 m^3/m^2 h bar [16]. For membranes with separation layers of Polyactive blended with 50wt% PEG high CO_2 fluxes of >2 m^3/m^2h bar could be achieved [14]. Further optimization of the composite membranes is required in order to provide membranes with sufficient long term stability. This work will be supported by tests under real conditions in strong collaboration with the researchers in Research Topic 3.

3.3. Research Topic 3: Process engineering and system integration

3.3.1. Reference power plants

As a conventional combustion plant the reference power plant NRW (RKW-NRW) has been chosen. A process model is set up in AspenPlus (Aspen Technology Inc.) and Pro/II (Simulation Science Inc.). The models include 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) are simulated. The simulated net efficiencies of 45.9 % (HC) and 44.5% (LC) provide a good match to the values given in the literature [19].
The integrated gasification combined cycle power plant in Puertollano has been 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 simulation $\eta_{LHV,MEM-BRAIN}$ = 50.31 % is comparable to the results of [20] $\eta_{LHV,Kloster}$ = 50.5 %. (excluding the auxiliary power consumption of the Air Separation Unit).

3.3.2. Post-combustion capture

The state-of-the-art capture scenarios indicate that post-combustion using chemical absorption plays a dominant role in current R&D activities with CCS. However, the inherent weaknesses: a) degradation of the solvent, leading to high material costs and high disposal costs, b) additional environmental pollution caused by the used solvents and c) high energy consumption for the solvent regeneration process, make it not a clear winner for the future application. Gas separation membrane capture used for post-combustion, as a competing technology, possesses the advantages of end-of-pipe application, and of less environmental impact than chemical absorption method [21], [22]. The compact and modular structure makes it flexible in use and could be a promising option as retrofit. Gas separation membranes used for post-combustion capture have been investigated by several groups independently [23-29].

On the basis of the results of the single-stage membrane [29], a cascade concept: using vacuum pump on the permeate side of the 1st membrane, compressor on the feed side of the 2nd membrane, simultaneously, recycling the retentate of the 2nd membrane to the flue gas feed side, shown in **Figure 7**, was developed and applied for 600 MW North Rhein-Westphalia reference power plant (RKW-NRW) [19] including CO_2 compression process (110 bar, 30°C). Using the update Polyactive® membrane developed by GKSS with CO_2/N_2 selectivity of 50 and CO_2 permeance of 3 $Nm^3m^{-2}h^{-1}bar^{-1}$ [30], the efficiency loss of the system is 6.5%-pts. under the separation target: 95 mol% CO_2 purity and 70% degree of CO_2 separation. This result was compared with a chemical absorption - MEA (monoethanolamine) absorption capture [31], [32], see **Table 1**, and shows a quite promising retrofit option for existing power plants.

Fig. 7: A cascade concept, recycling the retentate of the 2nd membrane to the feed of the 1st membrane

Table 1: Comparison between a cascade membrane concept with MEA absorption applied for 600 MW RKW-NRW, separated CO_2 compressed to 110 bar, 30°C [31], [32]. The feed flue gas is composed of 14 mol% CO_2 and 86 mol% N_2; the vacuum pressure of the 1st membrane is 100 mbar, the pressure level of the 2nd membrane is 4 bar; it is assumed that the efficiency of all compression machines is 85%.

3.3.3. Pre-combustion capture

The main competing technologies for carbon capture and storage by means of IGCC power plants are physical absorption processes like RECTISOL and SELEXOL. The literature shows that there is a huge data spread. Typically the calculated efficiency losses are around 9 to 11%-points, but there are also some studies showing losses like 5% [33 -35].

IGCC power plants offer certain advantages for the operation of membranes for CCS. There is a large driving force across the membrane because of the high absolute pressure of the syngas as well as the high partial pressure of the permeating species. This leads to low membrane areas and a compact equipment. Membranes operated in a 4-end module can significantly reduce the energy penalty caused by the compression unit of the CO_2.

In order to incorporate membrane simulations into the simulation software AspenPlus a FORTRAN code was developed. This code is able to simulate the mass transfer along the membrane as well as the heat transfer and the pressure losses for different forms of flow. Permeation simulations were performed with this code for polymeric membranes. The main polymeric membrane which was investigated was a Pebax®/PG50 described in the results of RT2. This membrane has a selectivity towards CO_2/H_2 of about 15. The membrane has to be operated as a 3-end module because a sweep gas would diminish the purity of the separated CO_2. Single membrane module concepts as well as cascade concepts have been examined. The results for CO_2 selective membranes show that with state of the art membranes (CO_2/H_2 selectivity 15.5) the current requirements concerning CO_2 purity and CO_2 separation degree can not be fulfilled. A CO_2/H_2 selectivity of 150 for a single CO_2 selective membrane would be needed to obtain power plant efficiency losses below 10% points with separation degrees above 85% (**Figure 8**). For a cascade concept the CO_2/H_2 selectivity needed would be in the order of 60 to achieve the same values.

Fig. 8: Results of single membrane concept simulations for the integration of polymeric membranes

As ceramic membranes described in the results of RT1 show better separation characteristics even higher separation degrees can be expected with comparable efficiency losses.

3.3.4. Oxyfuel combustion

The reference power plant (RKW-NRW) was modified to an oxyfuel process. Two different membrane integration concepts can be applied.

1. Four-end membrane module situated within the recirculation.
2. Three-end membrane module situated outside the recirculation as stand alone.

The main focus in the work at hand will be on the second concept since today available membranes have no chemical stability against CO_2 and SO_x [35], [36].

When applying the 3-end concept, the membrane is a stand alone unit. The membrane is fed by preheated air and on the permeate side vacuum is applied. The influence of the separation ratio and the vacuum and air pressure on the power plant efficiency will be shown.

Influence of the separation ratio and air- and vacuum-pressures

By modifying the oxygen separation ratio the applicable vacuum pressure can be elevated. The permeate pressure is limited by the oxygen partial pressure in the retentate: p_{O2},retentate always has to be greater than p_{O2}, permeate to guarantee a driving force over the membrane. By lowering the separation ratio the oxygen partial pressure in the retentate rises resulting in higher feasible vacuum pressures (cf. **Figure 9**). Permeate pressures up to atmospheric conditions can be applied. The optimum power plant efficiency can be reached at separation ratios between 60 and 70 %. For lower permeate pressures the main efficiency influencing parameter is the energy demand of the vacuum pump. The energy demand for vacuum above 500 mbar is almost constant. For higher permeate pressures and lower separation ratios (< 60%; cf. Fig. 3: separation ratio 50%) the dominating efficiency influencing parameter changes. With a lower separation ratio the amount of waste heat rises and interferes the positive effect of the lower energy demand of the vacuum pump. A similar characteristic can be identified for feed pressures of 15 and 20 bar (cf. **Figure 10**). For higher feed pressures this effect occurs at higher separation ratios since the influence of the vacuum pump on the overall efficiency is lower. For a medium heat integration level minimal efficiency drops of 6.2 %-points can be reached.
Compared to the efficiency drop of Oxyfuel-Processes with integrated cryogenic air separation ($\Delta\eta$ = 8 - 11 %-points) [38], [39] the membrane based oxyfuel process has the potential to decrease the efficiency drop by 2 - 5 percent

Fig. 9: Influence of the separation ratio and the permeate pressure on the efficiency of an oxyfuel power plant (1210 MWth) at 10 bar feed pressure.

Fig. 10: Efficiency drop of an 3-end oxyfuel power plant at different feed pressures and separation ratios.

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 most important parameter for the subsequent processes compression, transport and storage are the impurities of the CO_2 stream. Technical, chemical or physical effects of various impurities for compression, transport, storage and health security are investigated. The multi-component 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. In a detailed assessment of compression processes for typical Oxyfuel and IGCC flue gases different compression and purification systems (distillation column versus flash drum) are compared. The results show the relation between increasing energy requirement to reach a higher CO_2 purity and higher storage capacity depending on the impurities of the flue gas. Exemplarily, **Figure 11** shows the compression work and storage capacity for an IGCC-off gas. An optimization between compression work demand and purity is necessary.

Fig. 11: Compression work and storage capacity for an IGCC-off gas [40]

Contaminations might also lead to an unwanted phase change depending on temperature and pressure. With respect to transport, this phase change can yield in an increasing volume and therefore leads to higher energy demand for pumping. Other impurities are restricted due to their high corrosion potential, toxicity or hydrate formation potential. Various restrictions to impurities are defined by CO_2-pipeline operators in the US [41 -43].

Impurities can also decrease the level of utilization of the storage capacity and might change the storage geology. In December 2008 an EU directive for "Geological storage of carbon dioxide" [44] was launched. However, the definition of the CO_2 stream quality is still unspecific. It states that a CO_2 stream shall consist "overwhelmingly" of carbon dioxide. Additionally, purity requirements have to be set up in further national agreements. No general or principal restrictions can be given as every storage site has its specific environment [3].

3.4.2. Screening LCA for membranes and power plants and resource balances

For a comprehensive evaluation of environmental impacts a solely consideration of CO_2 emissions is not enough. Additional up and downstream processes, such as coal extraction and supply or waste treatment, must be integrated. Furthermore, other emissions and associated environmental impacts arise also from the application of CCS technology. One methodology to cover these aspects is the Life Cycle Assessment (LCA), where the technology with all up and down streams is evaluated [45]. Membrane technology competes with other capture technologies. One advantage of membranes is assumed to be the environmental performance. To show whether this is true considering all environmental aspects, the developed membrane systems (RT 1-3) have to be compared with other CCS technologies. For each process route the currently most promising membrane technology and a competing technology is selected (**Figure 12**).

Fig. 12: Comparison of different CCS technologies

The results obtained in the process simulation (RT 3) are transformed into life cycle data and integrated into an environmental calculation software. The process data are combined and completed by data considering upstream and downstream processes, such as coal supply or waste treatment, taken mostly from the ecoinvent 2.01 database [46]. For each process the important input and outputs are determined and the potential impacts connected with the production of 1 kWh_e are assessed. Typical impact categories beside global warming potential are acidification, eutrophication, human toxicity but also resource use. **Figure 13** shows an exemplary preliminary result of the impact assessment for the Oxyfuel process route.

Fig. 13: Life Cycle Impact Assessment for four different power plant concepts: Reference power plant NRW, ultra-supercritical power plant, cryogenic air separation and the three-end membrane system

Compared are four systems with and without CO_2 capture. As a reference system the reference power plant NRW is chosen (see 3.3.1). The development of power plant technology without CCS is accounted for in the simulation of an ultra-supercritical power plant concept (USC, 700°C, 350 bar) [47]. CCS technology concepts considered are the cryogenic air separation and the three-end membrane system described above.

As expected, the Global Warming Potential GWP decreases due to efficiency increase for power plants without CCS. With capture technology the decrease is even more considerable, although it is smaller than the estimated capture rate. This is due to the additional demand of coal supply, which is connected with higher methane emissions during mining. For the other impact categories the differences are mainly related to the efficiency of the plants.

Other CCS technologies, especially those using solvents, show a stronger increase in other impact categories [48-51]. For all three CCS routes the results for the competing technologies have to confirmed and compared to those for the selected membranes systems. Thus development targets can be defined and weak point analysis will contribute to further developments.

A major research task will be the analysis of the construction of the membrane system. Investigation about the construction and dismantling of a MEA plant show negligible impacts (< 0.5%) compared to the operation phase [52]. It has to be analysed whether this is also true for membrane systems.

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 against 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 [53], scenarios are generated that permit CCS to be classified within the framework of a national mitigation strategy for Germany until 2050.

Fig. 14: German power plant capacity meeting a 69 % CO2 reduction target until 2050

Figure 14 shows the development of German power plant capacity assuming a CO_2 reduction target of 69%. To meet this target the installed capacity increases by 50 %. The results show that CCS is an interesting option in Germany, especially for lignite-based power production. About 27 GW lignite fired power plants have to be installed (including 7 GW retrofitted power plants) in the year 2050. The capacity of hard coal fuelled plants with CCS is 7 GW (all retrofitted). The calculated capacity building rates for CCS are high and imply additional lignite supply infrastructure. Assuming an average membrane capacity of 1 m^2/kW the calculated built up of capacity requires an annual membrane production of up to 2 Million m^2.

To achieve the same 69% reduction target without CCS technology other, more expensive measures (in other sectors) are necessary, which increase the total CO_2-reduction costs for the total German energy system by about 27 Billion €/a in 2050. These results are strongly dependent on cost assumptions (investment costs, energy prices). However, sensitivity analysis has proven a robustness of the findings.

4. Acknowledgements

Financial support from the Helmholtz Association of German Research Centres (Initiative and Networking Fund) through the MEM-BRAIN Helmholtz Alliance is gratefully acknowledged.

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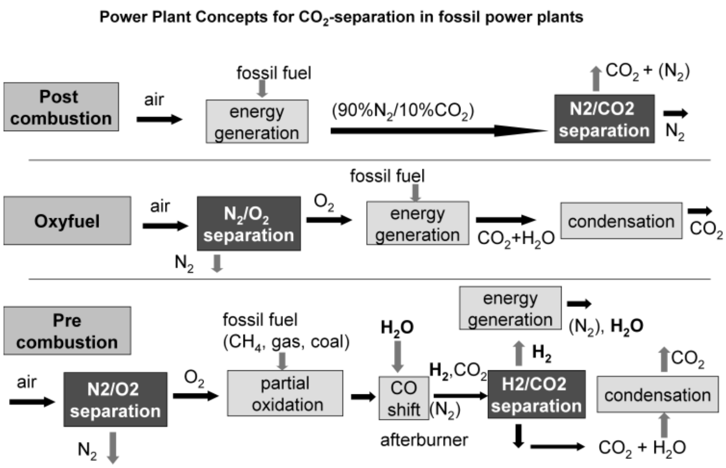
6. Figures



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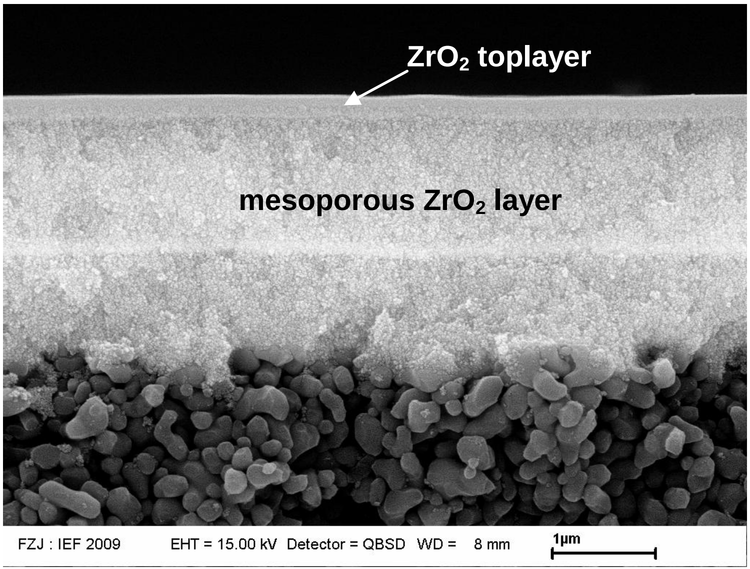


Fig. 2: Microporous ZrO_2 membrane on top layer of a high quality mesoporous ZrO_2 layer

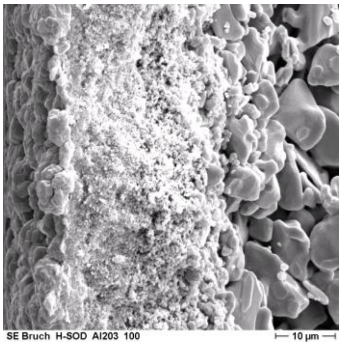


Fig. 3: SOD membrane layer on top of an α-Al_2O_3 support disc

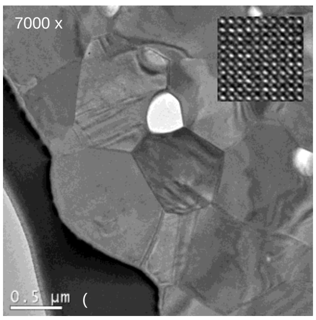


Fig. 4: HTEM of perovskite

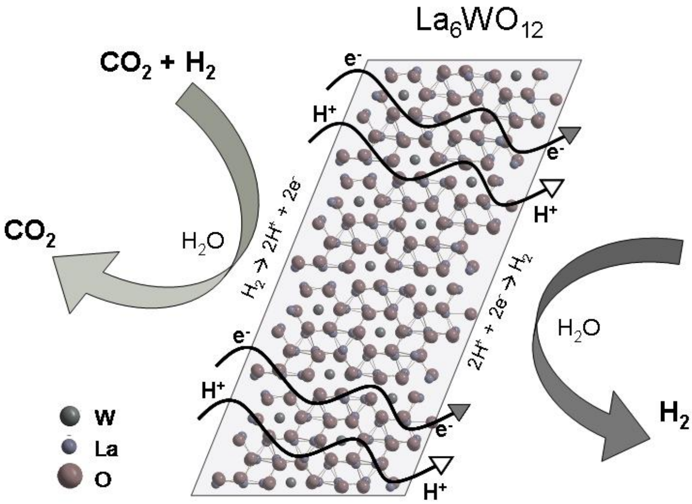


Fig. 5: Scheme of the permeation process in a mixed protonic-electronic conducting membrane made of La_6WO_{12}

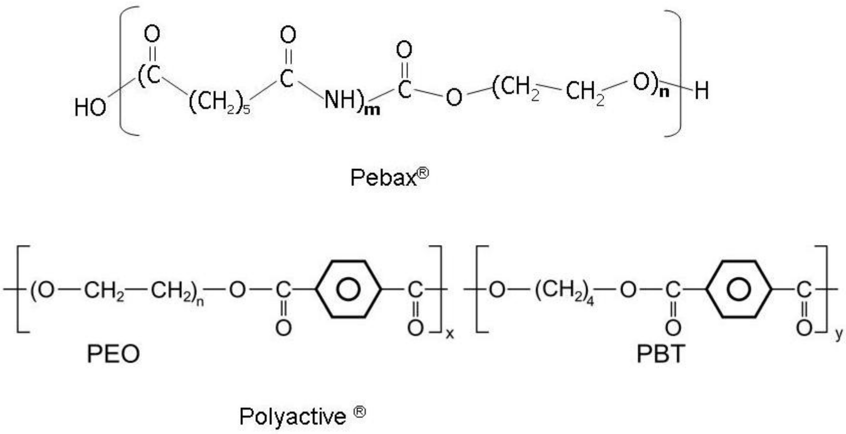


Fig. 6: Structural formulaes of Pebax® and Polyactive®

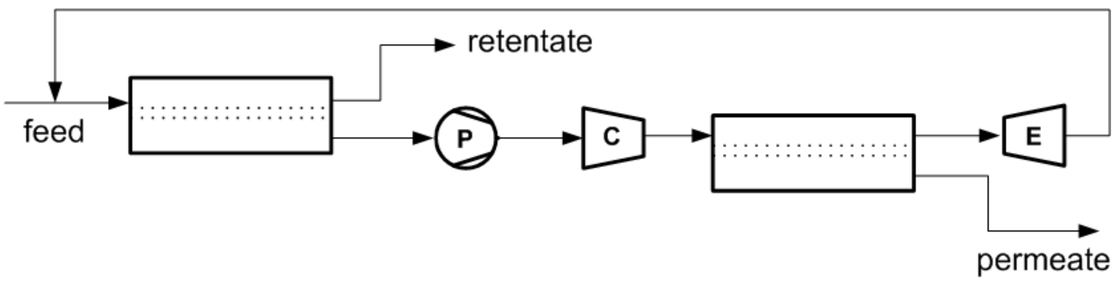
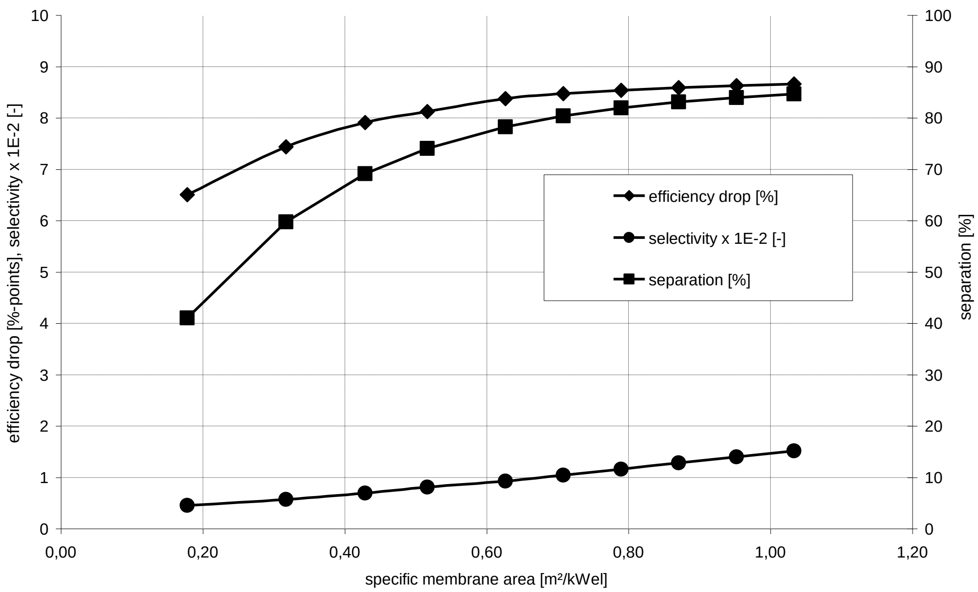


Fig. 7: A cascade concept, recycling the retentate of the 2nd membrane to the feed of the 1st membrane



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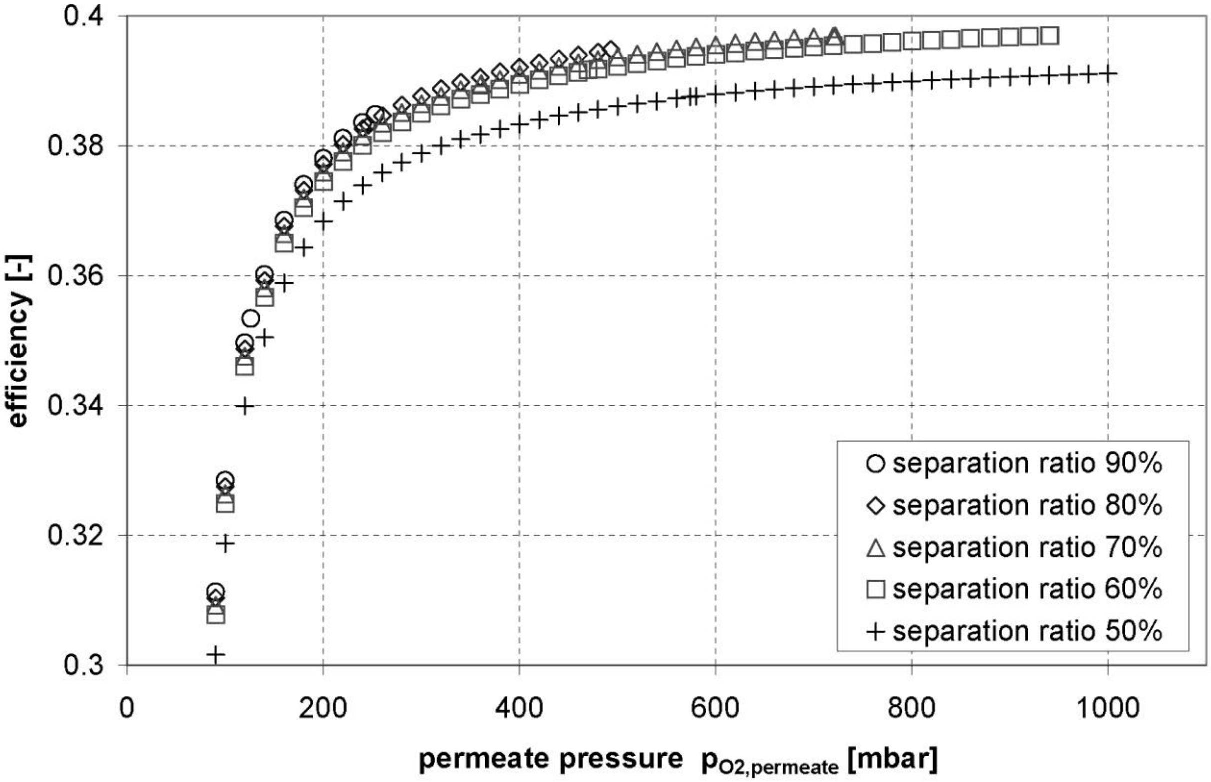

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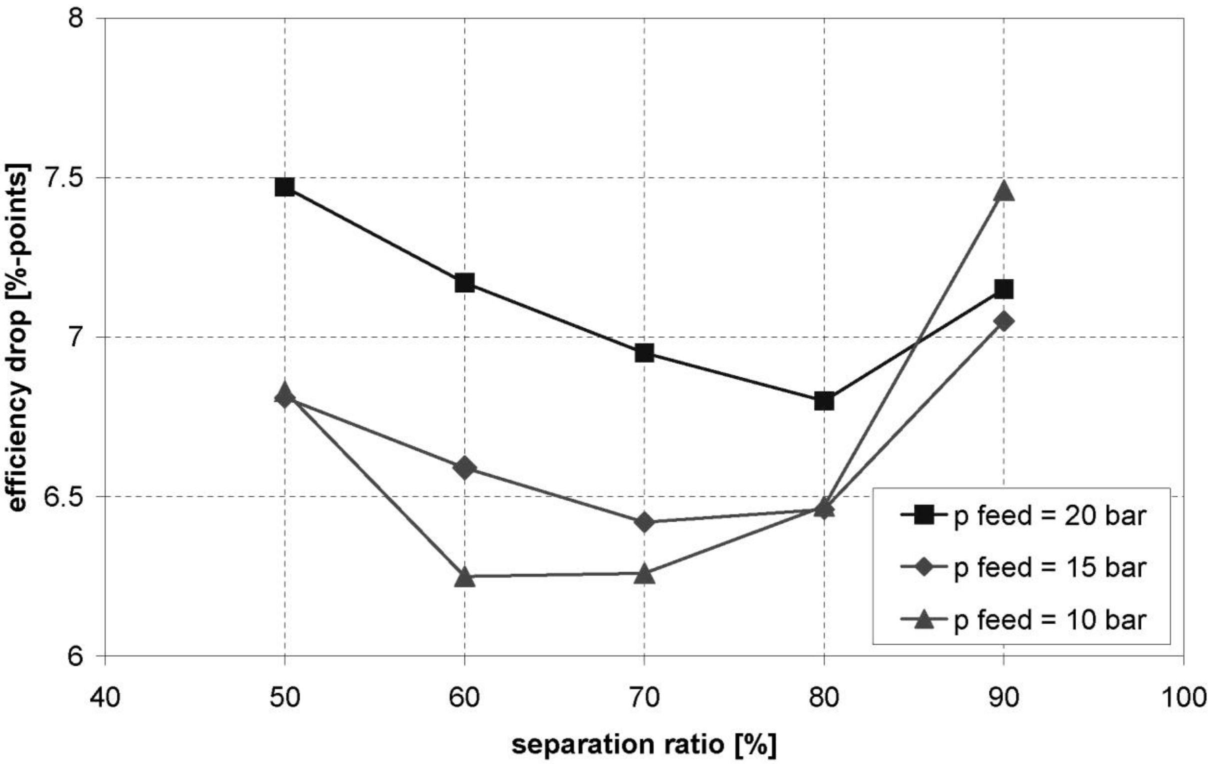

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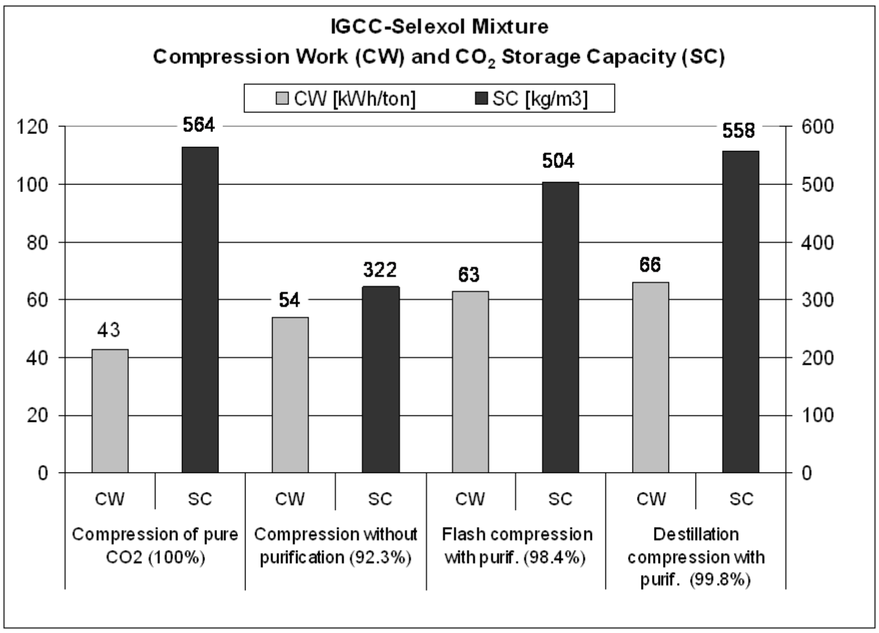

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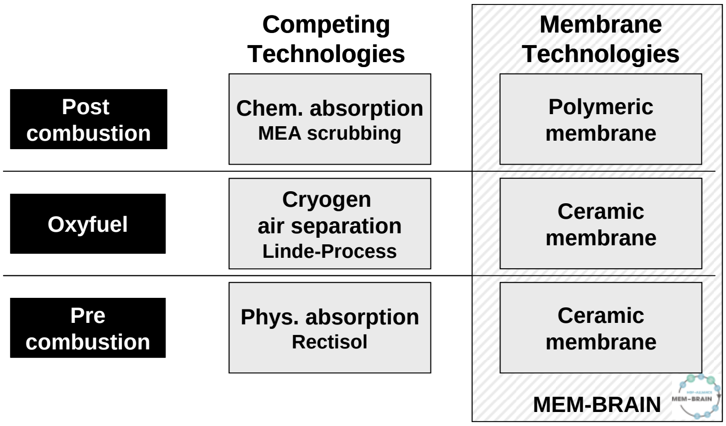

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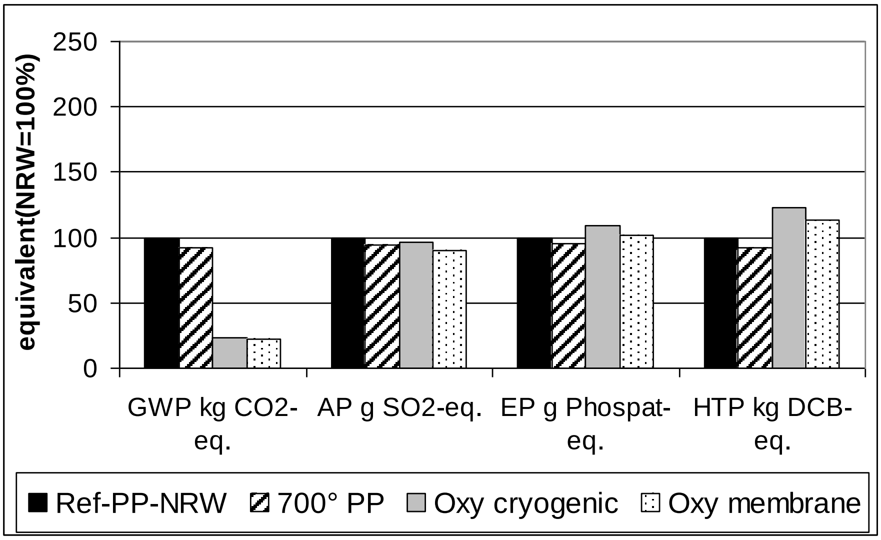


Fig. 13: Life Cycle Impact Assessment for an Oxyfuel process using membrane technology

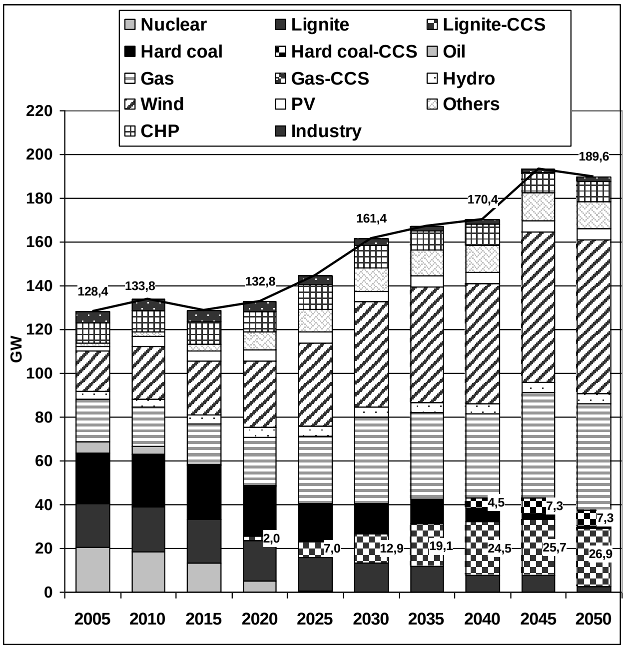


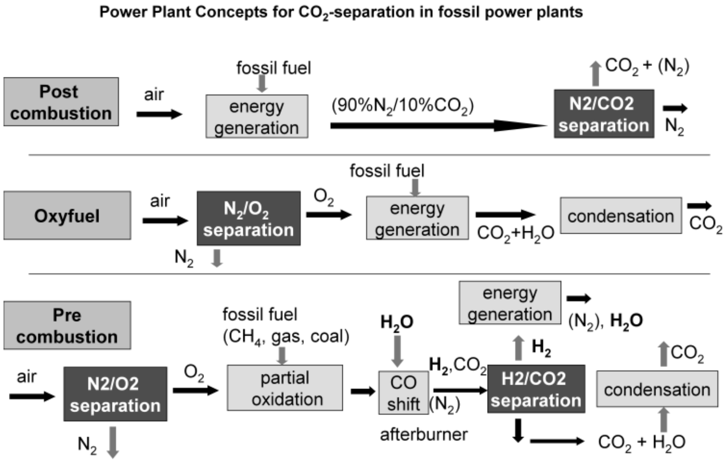
Fig. 14: German power plant capacity meeting a 69 % CO_2 reduction target until 2050

7. Tables

Table 1: Comparison between a cascade membrane concept with MEA absorption applied for 600 MW NRW-RKW, separated CO_2 compressed to 110 bar, 30°C [29], [30]. The feed flue gas is composed of 14 mol% CO_2 and 86 mol% N_2; the vacuum pressure of the 1st membrane is 100 mbar, the pressure level of the 2nd membrane is 4 bar; it is assumed that the efficiency of all compression machines is 85%.

Capture method	Separation degree [%]	CO_2 purity [mol%]	Specific energy for capture [kWh/$t_{separated\ CO2}$]	Specific energy for compression [kWh/t_{CO2}]	Efficiency loss [%-pts.]
MEA absorption	70	99	220	100	**8.2**
Cascade membrane	70	95	151	105	**6.4**

6. Figures



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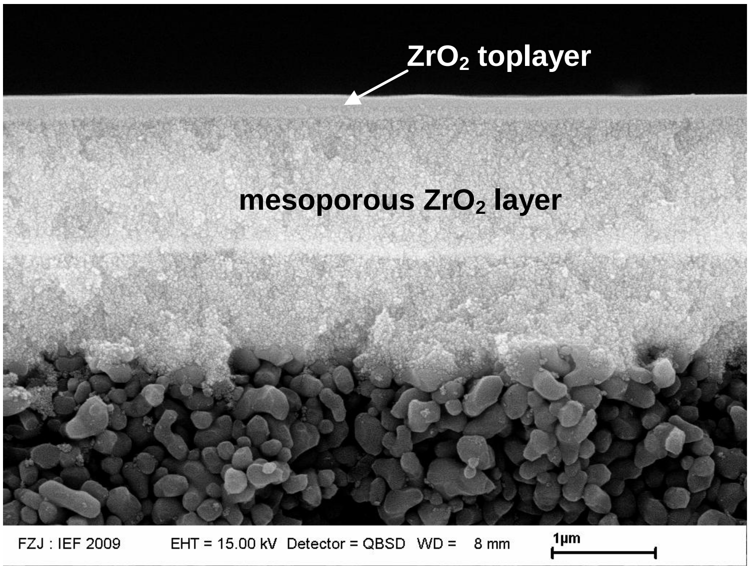

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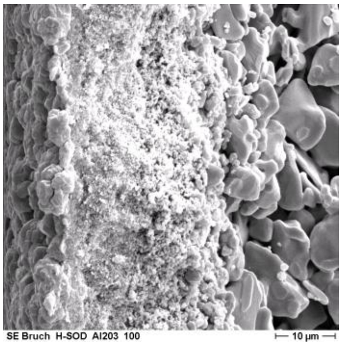

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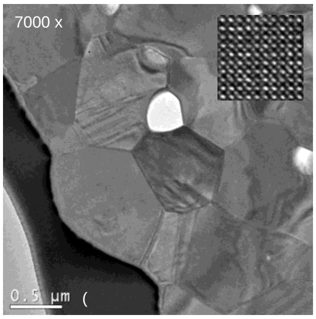

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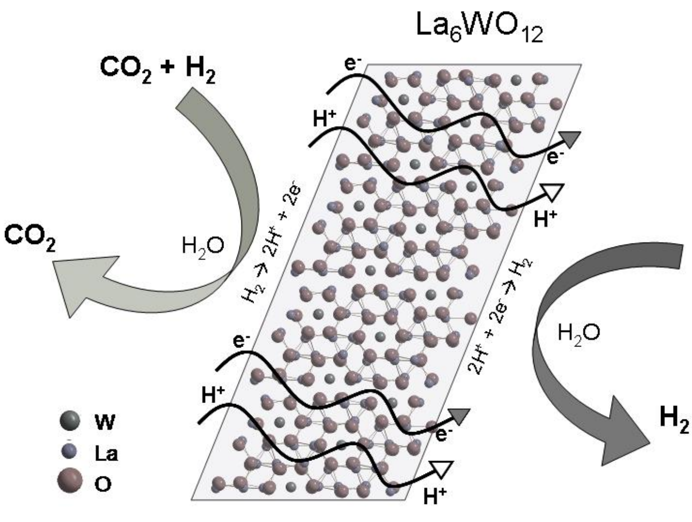

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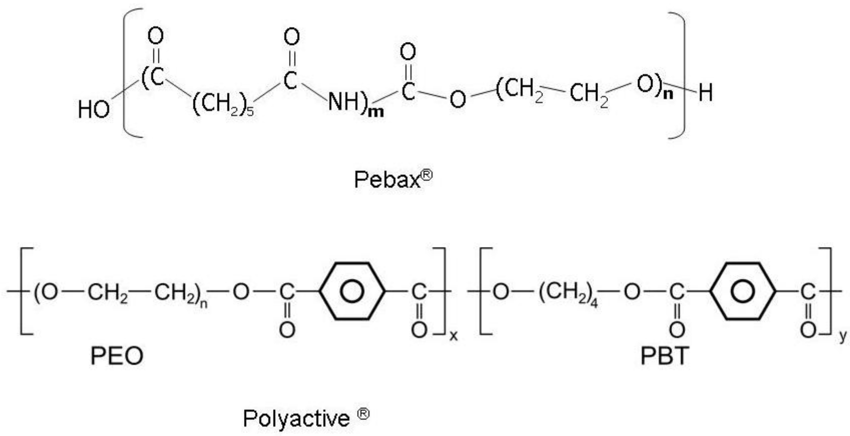

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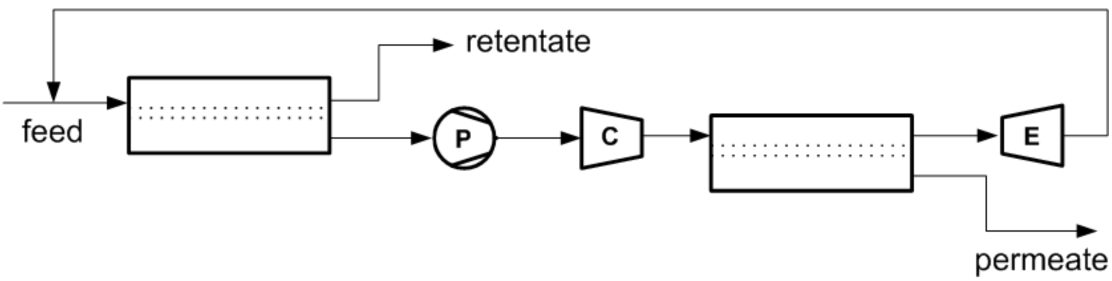

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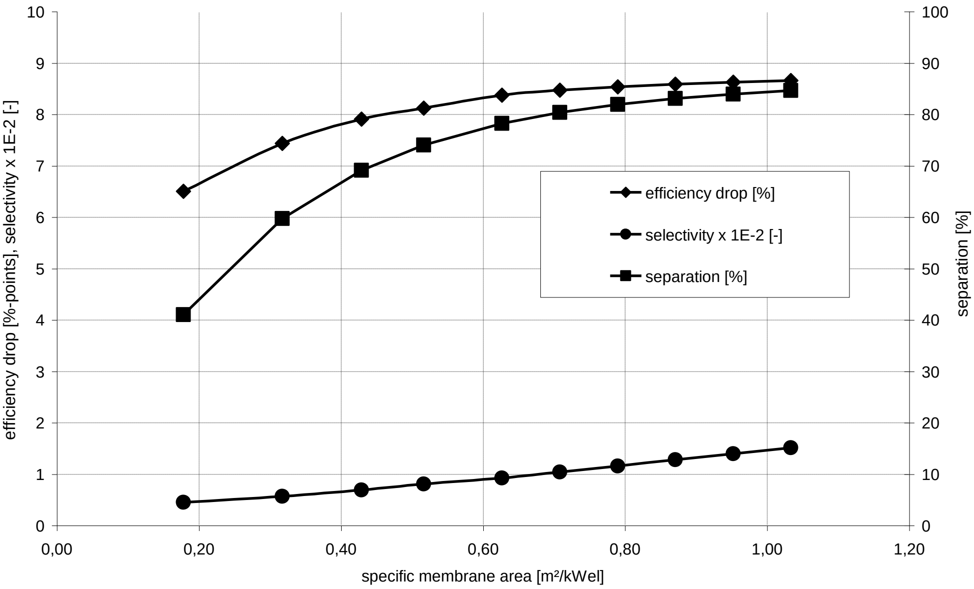

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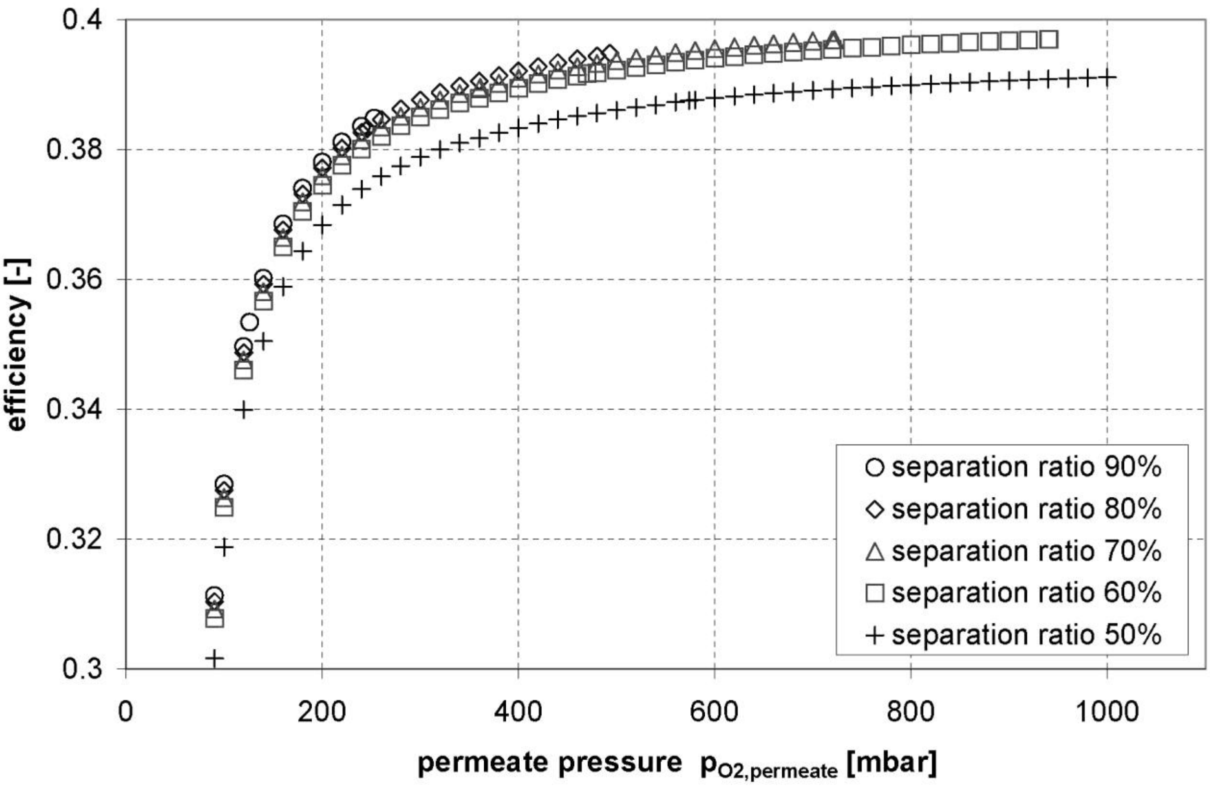

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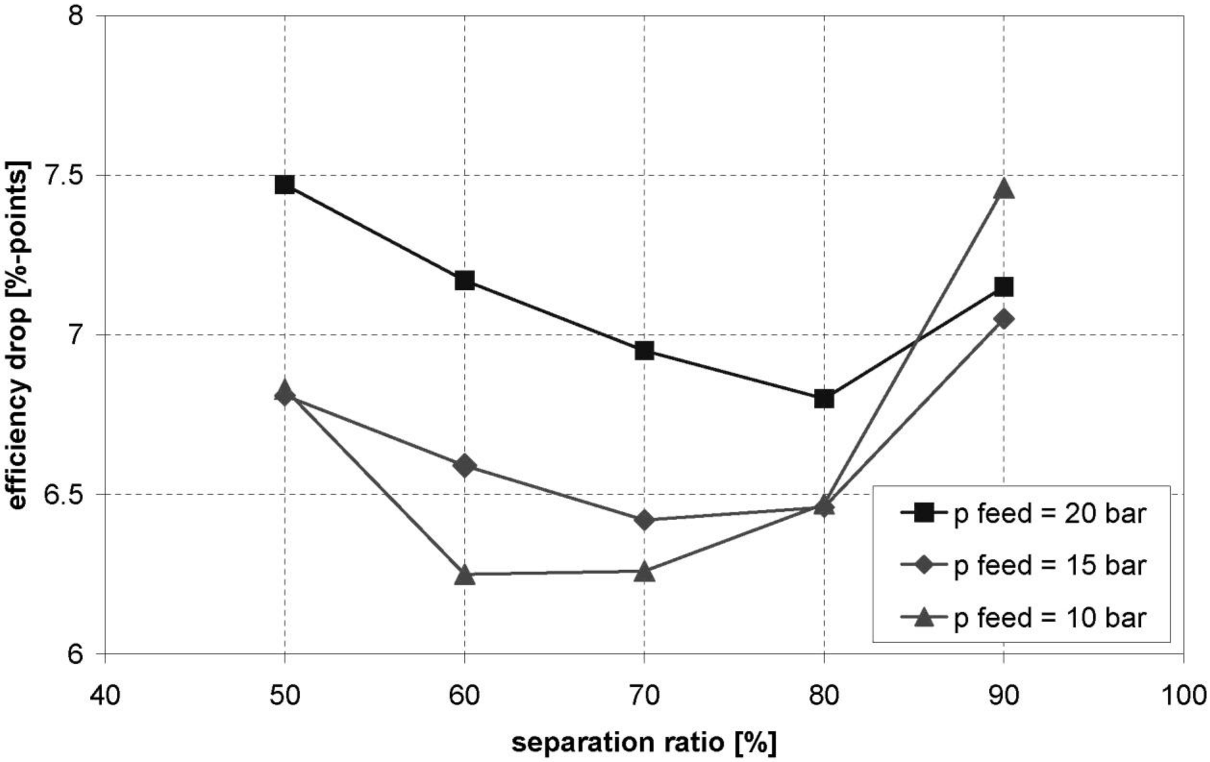

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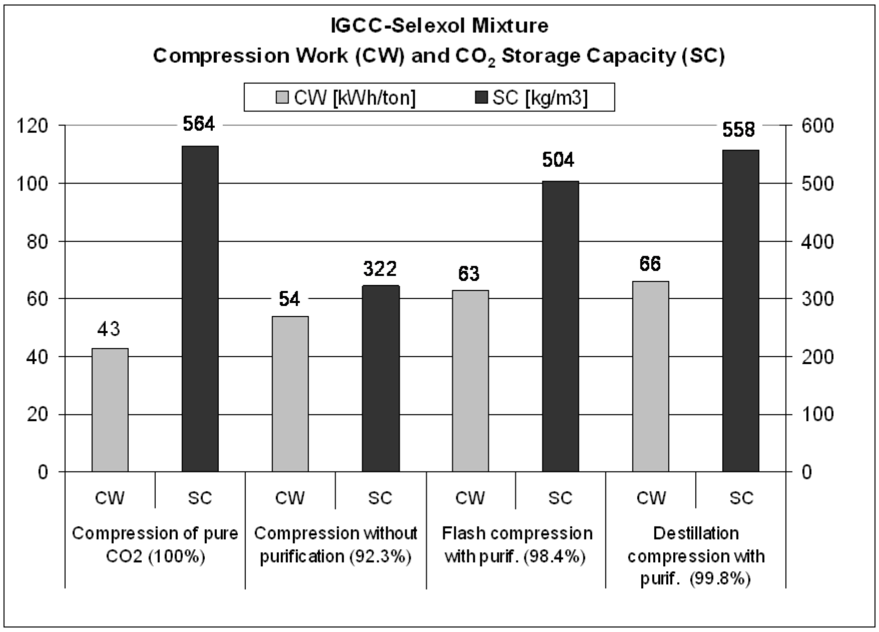

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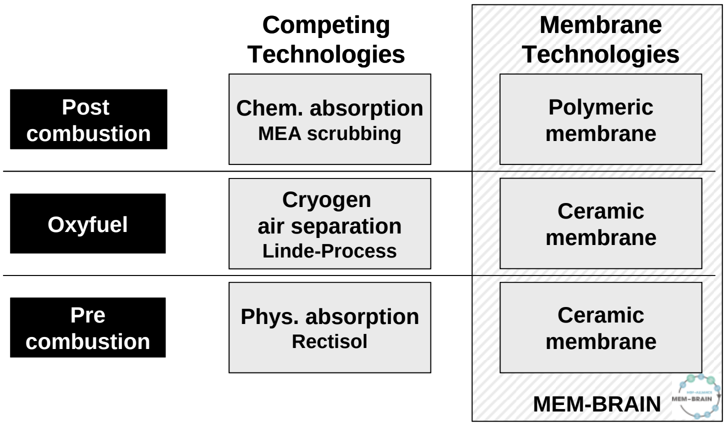

Fig. 12: Comparison of different CCS technologies

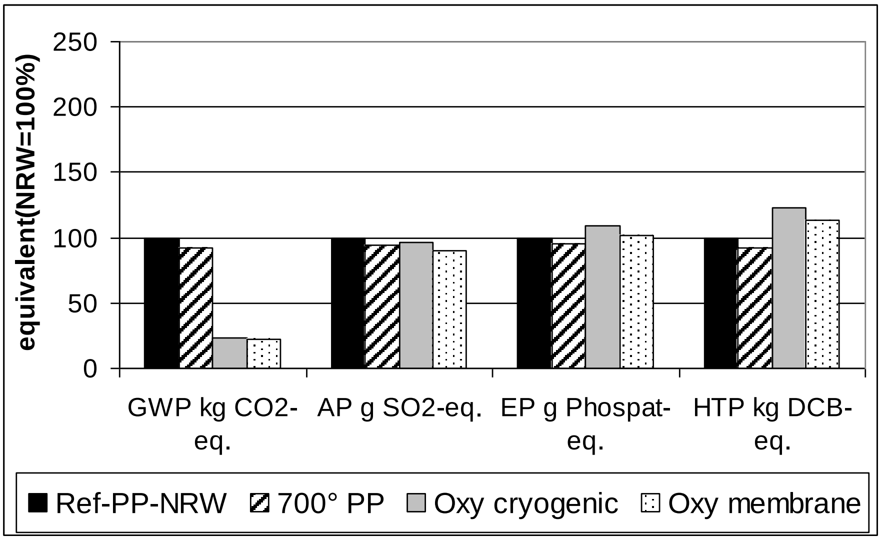

Fig. 13: Life Cycle Impact Assessment for an Oxyfuel process using membrane technology

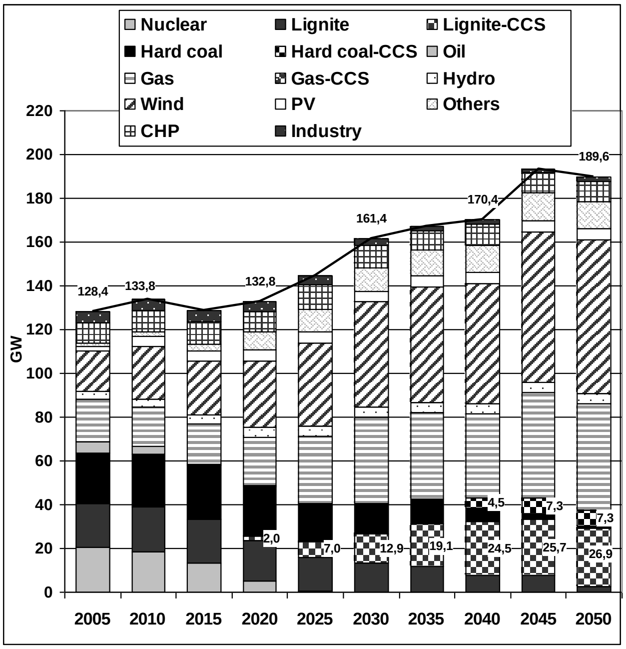

Fig. 14: German power plant capacity meeting a 69 % CO_2 reduction target until 2050

Table

Gas separation membranes for zero-emission fossil power plants: MEM-BRAIN

M. Czyperek[a]*, P. Zapp[a], H. J. M. Bouwmeester[b], M. Modigell[c], K. Ebert[d], I. Voigt[e], W. A. Meulenberg[a], L. Singheiser[a], D. Stöver[a]

[a]*Forschungszentrum Jülich GmbH, Institute of Energy Research, Leo-Brandt-Str. 1, D-52425 Jülich, Germany*
[b]*University of Twente, Department of. Science and Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands*
[c]*RWTH Aachen University, Department of Chemical Engineering, Turmstr. 46, D-52056 Aachen, Germany*
[d]*GKSS-Forschungszentrum Geesthacht GmbH, Institute of Materials Research, Max-Planck-Str. 1, D-21502 Geesthacht, Germany*
[e]*Hermsdorfer Institut für Technische Keramik e.V., Michael-Faraday-Str. 1, D-07629 Hermsdorf/Thuringia, Germany*

7. Tables

Table 1: Comparison between a cascade membrane concept with MEA absorption applied for 600 MW NRW-RKW, separated CO_2 compressed to 110 bar, 30°C [29], [30]. The feed flue gas is composed of 14 mol% CO_2 and 86 mol% N_2; the vacuum pressure of the 1st membrane is 100 mbar, the pressure level of the 2nd membrane is 4 bar; it is assumed that the efficiency of all compression machines is 85%.

Capture method	Separation degree [%]	CO_2 purity [mol%]	Specific energy for capture [kWh/$t_{separated\ CO2}$]	Specific energy for compression [kWh/t_{CO2}]	Efficiency loss [%-pts.]
MEA absorption	70	99	220	100	**8.2**
Cascade membrane	70	95	151	105	**6.4**

* M. Czyperek. Tel.: +49-2461-61-5450; fax: +49-2461-61-2455.
E-mail address: m.czyperek@fz-juelich.de