

PROJECT FINAL REPORT

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Content

<u>Final publishable summary report</u>	3
Executive summary	3
Summary description of project context and objectives	4
Rationale	4
General concept	4
Objectives	6
Description of the main S&T results/foregrounds	8
WP1: Synthesis and characterization of poly(ionic liquids)	8
WP2: Characterization and functionalization of enzymes	12
WP3: Gas separation membranes	17
WP4: Absorption in columns	20
WP5: Absorption in membrane contactors	26
WP6: Process development	30
WP7: Assessment of new technologies in industrial application scenarios	34
<u>The potential impact and the main dissemination activities and exploitation of results</u>	39
Improved materials and production techniques for a targeted functionalization of tailored gas separation membranes	39
Innovative concepts for enzyme application in gas-liquid contacting systems	40
Innovative energy and resource efficient process concepts for post combustion carbon capture	42
Impact on global market	42
Technological impacts and risks	43
European Transnational Approach	43
<u>Use and dissemination of foreground</u>	44
Section A – Dissemination measures, including any scientific publications relating to foreground	44
Section B – Exploitable foreground and the plans for exploitation	46
<u>Report on societal implications</u>	65

Final publishable summary report

Executive summary

INnovaTive Enzymes and polyionic-liquids based memBRAnes as CO₂ Capture Technology (INTERACT) was a collaborative research project aiming at the investigation and development of new means for post combustion CO₂ capture. The complex task was addressed with a comprehensive multiscale methodology that started with the development of economic synthesis techniques for the production of innovative and highly selective poly(ionic liquid)s (PILs) and enzyme-solvent systems. The results of the sophisticated material design and characterization of the developed materials were further incorporated in highly effective gas separation membranes and absorption systems based on packed columns and membrane contactors. Extensive experimental investigations from lab-scale to technical and pilot-scale were performed to demonstrate the implementation of the newly developed technologies, while detailed performance models were developed for each technology in order to aid the experiments and determine optimal operating conditions. Finally a variety of process concepts was developed based on the newly developed technologies and a process-wide evaluation of the potential impact was performed, taking into account the integration with the power plant and techno-economic as well as environmental criteria for the evaluation. The technical work was structured in seven work packages, which can be clustered in two material design and characterization work packages, three technology-focused work packages and two process related work packages. While the three clusters started in a staggered fashion, in order to account for the necessary information transfer from bottom to top, there was also a severe overlap of the processing periods of the three clusters, in order to allow for feedback and recourse from top to bottom. Consequently, the complete development process was highly integrated. Within the material design work packages a multitude of different PILs were developed and effective production processes were designed to produce the most promising materials in a capacity of up to 100kg. The most selective porous and dense PILs proved to be competitive sorbents for the use in adsorption processes as well as highly selective active layers in thin film composite gas membrane processes respectively. A full characterization of enzyme-solvent systems allowed for the identification of highly efficient systems in which the enzyme significantly enhances mass transfer in absorption processes. This makes it possible to exploit solvents with significantly lower heat requirements for regeneration. Furthermore, the combined effort of the material design and technology work packages made it possible to design tailored membrane contactors, which exploit both a selective PIL coating in combination with an enzyme enhanced solvent system in order to maximize the synergetic benefits and improve mass transfer in absorption processes. For each of the newly developed technologies suitable process concepts were developed in order to exploit the potential benefits, while simultaneously taking into account the additional restrictions introduced by the novel materials. These concepts were evaluated in the scope of an industrial CO₂ emission scenario, whereas detailed techno-economic and environmental evaluations showed that the newly developed technologies do not only provide the potential to significantly reduce the environmental impact of coal-fired power plants and other CO₂ emitting processes, but also outperform the current state-of-the-art amine scrubbing process.



**Innovative enzymes and
polyionic-liquids
based membranes
as CO₂ capture technology**

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Summary description of project context and objectives

Rationale

In the last decades, CO₂ capture gained significant attention to minimize the environmental impact of post-combustion processes, while conventional technologies like chemical scrubbing with amines face severe economic boundaries due to their high energy consumption. Novel materials, such as (poly(ionic liquid)s (**PILs**) and enzymes) implemented into innovative technologies (e.g. membrane contactors) can provide a promising solution, to reduce the associated energy penalty and the cost of carbon capture. Exploiting the synergies between the high CO₂ capture affinity of the materials and the intensified technologies can facilitate the effort to make CO₂ capture industrially feasible in the future.

General concept

The general aim of INTERACT was to investigate and introduce new means to capture CO₂ in the post combustion process. Therefore developments of both, PILs and enzymes, as well as their integration into membrane and/or absorption systems was pursued. In-depth investigations of these separation technologies were performed in order to determine their performance with regard to separation effectiveness, durability, scale-up and finally, when embedded in suitable process concepts, techno-economic and environmental performance. Consequently, extensive experimental investigations were augmented with sophisticated and rigorous modelling, which was finally utilized to perform conceptual design studies for the development of optimized process concepts, which were to be rated by techno-economic as well as environmental criteria, making use of a detailed life cycle analysis. While the environmental benefit from CO₂ capture technologies does not stand to question, the currently favored chemical solvent scrubbing based on activated amine solutions, suffers from a high energy requirement for solvent recovery, as well as solvent degradation, resulting in high capital costs as well as an energy penalty of about 30 – 40%. The general concept of this project was to open new pathways for the development of novel high-potential processes for post combustion CO₂ capture based on new materials, in order to significantly reduce the energy penalty, as well as capital and operating costs associated with the CO₂ capture process. Therefore, INTERACT combined two different classes of key materials integrated into three intensified technologies to enable synergy effects which provide promising new alternatives and “proof of concept” for CO₂ capture. The innovative technologies were developed and tested to realize the “proof of concept” by demonstrating experimentally the feasibility and performance of the new CO₂ capture prototype technologies and to show their economic benefits compared to conventional state-of-the-art processes by model-based analysis.

Materials

In the INTERACT project a variety of **dense and highly porous PILs** were synthesized and studied in a variety of CO₂ capture strategies, designed e.g. as active separation layers in thin film composite membranes, that enables the possibility to integrate the CO₂ affinity of the PIL in the membrane in order to enhance CO₂ permeability and selectivity. With additional additives it was possible to synthesize material formulations that are located close to the upper bound on the Robeson plot. The other material-focused idea in INTERACT was to use the **enzyme carbonic anhydrase**, a nature originated bio-catalysts that handles CO₂ in most mammals and other lifeforms, as an accelerant to support the CO₂ absorption. This opens the opportunity to use solvents with a significantly lower desorption temperature, and thereby lower energy penalty of carbon capture. Several suitable enzyme-solvent systems have been identified and the improvements and restrictions of enzyme implementation have been quantified. Overall it was shown that a significant reduction of the energy penalty by several percent points should be feasible in a suitable process concept accounting for the restrictions of enzyme implementation.

Technologies

The **tailored gas separation membranes** in INTERACT consist of a porous support layer, coated with a dense PIL layer. The PIL layer preferably adsorbs CO₂, whereas the CO₂ subsequently desorbs due to the partial pressure difference on the permeate side of the membrane and hence is transported through the membrane. Support layers were carefully designed from different materials, accounting for porosity, as well as chemical and mechanical stability and taking into account to produce the thin film composite membranes, including *in-situ* polymerization as well as dip or spray coating. The separation performance was further characterized and several configurations, including flow patterns and possible means for establishing the driving force have been evaluated in process design.

Absorption

In INTERACT a combination of the classical **chemically enhanced absorption** process with new solvent systems exploiting the possible rate-enhancement by **enzymes** was investigated. Enzymes were either dissolved in the solvent systems, or immobilized in catalytic packings as well as other forms of immobilization. Application of enzymes in **absorption columns** was proven at different scales, from small lab-scale to large pilot scale set-ups, and the obtainable rate-enhancements have been demonstrated for solvent systems with dissolved enzyme as well as different forms of immobilized enzyme. Besides the application of classical columns furthermore the application of **membrane contactors** was considered for absorption. Membrane contactors can overcome some of the major drawbacks of columns, since they present a physical barrier between gas and liquid phase allowing a dispersion free contact, while providing an extremely high specific surface area. However, the membranes cause an additional mass transfer resistance and sensitivity towards fouling, resulting in a limited lifetime¹, which has to be considered in a careful selection membrane materials. Besides the direct application of enzyme-activated solvents in non-selective membrane contactors a further integration of the innovative materials was considered in the INTERACT project, whereas a porous membrane was coated with a PIL layer in order to exploit the benefit of both materials, resulting in an enhanced driving force across the membrane for the hybrid membrane contactor. Since harsh desorption conditions may result in a deactivation of the enzymes, several desorption strategies were further carefully investigated, including the aforementioned avoidance of enzyme in the stripper by either immobilization of the enzyme in the absorber or recovery of the enzyme prior to the stripper by e.g. ultrafiltration membranes. A variety of different process concepts was developed, including the integration with the power plant and an evaluation of the options based on techno-economic as well as environmental performance.

Synergies

The project structure allows for the exploitation of synergies at different levels (see Figure 1). At the technical level the addition of a PIL-based layer on a support is one of the key ideas to perform a targeted functionalization of gas membranes and membrane contactors for selective removal of CO₂. The integration of enzymes into absorption columns allows for the exploitation of solvents which require less energy for the recovery in desorption without losing the efficiency of reactive solvents such as amines. Integrating enzymes into non-selective membrane contactors exploits the large surface area created by the membrane resulting in more **compact equipment**, while the implementation of a selective PIL coating combines the large surface area of the membrane and the selective and highly efficient enzyme systems with the driving force enhancement by the PIL layer. However, besides these technical advances, synergies on the knowledge level can be exploited due to the collaboration of experts from various research fields, bridging the gap between material designs, technology development and process engineering in order to determine an optimized solution for post combustion CO₂ capture.

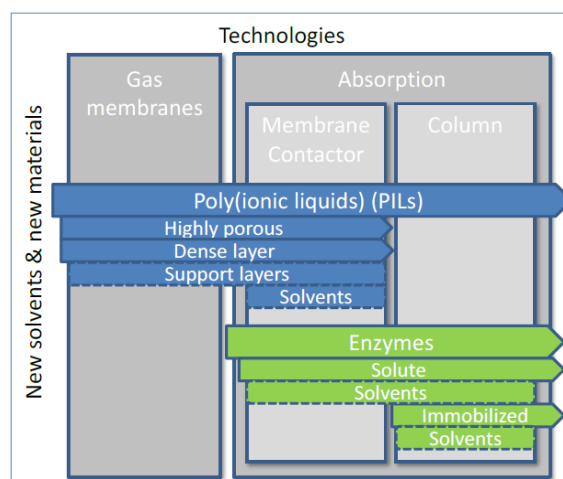


Figure 1: Conceptual approach of the INTERACT project

Objectives

The major project objectives of the INTERACT project were the

1. Targeted enhancement of CO₂ removal by the development of functionalized stable novel sorbent materials to aim for overall cost savings of 50% compared to a benchmark absorption column process using MEA as solvent.
2. Increased mass-transfer intensity in terms of increasing capacity of the solvent by up to 30% and enhancing mass transfer kinetics by at least a factor of 2 compared to the non-activated system by identifying novel stable biological activators in solvents based on reliable and robust datasets.
3. Development of highly efficient and stable recovery systems for activators and functionalized materials by immobilization or use of additional membranes.
4. Targeted creation of large phase contact areas.

These objectives were pursued by investigating innovative technologies, including gas separation membranes functionalized by a dense layer of PILs, absorption columns using enzyme activated solvents and immobilized enzymes and membrane contactors using enzyme activated solvents, as well as membrane contactors functionalized by a layer of poly(ionic liquid)s using conventional solvents as well as enzyme activated solvents

Only the most promising ones evaluated by simultaneous analysis of these technologies through calculations of energy penalty and economics were to be tested and validated as “proof of principle” by prototype testing in order to overcome the following technical and economic challenges:

1. Lack of reliable data on materials and their interaction with support materials in operation.
2. Lack of robust and reliable models, considering chemical reaction, fluid flow, mass transfer and energy transport
3. Lack of detailed understanding of key-technologies required for process design
4. Lack of strategies for effective integration of materials and scale-up of equipment

In order to overcome these challenges, the INTERACT project aimed at breakthroughs in the key activity areas of its integrated R&D-framework. More specifically, breakthroughs in the following scientific and technical domains were targeted:

1: New materials

Milestone: Enabling new materials for CO₂ capture by the development of stable poly(ionic liquid) layers at lab-scale, the identification of stable combinations of IL-PIL-solvent-enzyme-membrane systems as the basis for the integration into INTERACT technologies: gas

separation membranes, membrane contactors with and without enzymatic solvents *and for testing at larger scales by the establishment of dedicated processing*. After the identification of the ILs to PIL's (and blends of PIL's with IL and salts), the most suitable materials for CO₂ absorption are to be tested as either highly porous materials or dense layers, integrated in gas separation membranes and membrane contactors. Different set of IL's/PIL's may be selected, while only the most promising are to be tested to account for different CO₂ capture technology requirements.

2: New equipment for the technologies

Milestone: *Development and testing of stable enzyme-activated new column internals at different scales, including laboratory scale-columns (Diameters < 25mm) and scalable pilot-columns (Diameter = 100mm).* Enzymes will be investigated in solution as well as immobilized, taking into account surface coatings of packings and implementation of enzyme beads embedded into envelopes into structured packings. The immobilization should allow for good contact between enzyme solvent and gas, while avoiding enzyme transfer to the desorber. Enzyme activity, loss and CO₂ recovery rates are to be evaluated and the most promising enzyme supported CO₂ absorption method in columns will be defined with regard to energy penalty and stability.

3: New technologies

Milestone: *Development of new capture technologies exploiting synergies of enzymes and PILs with novel gas separation membranes and functionalized membrane contactors.* Based on the newly developed materials, gas separation membranes as well as membrane contactors will be functionalized with PIL layers to enhance their performance. The complex interactions between the PIL layer and membrane support need to be fully understood to prevent leaching and other stability problems, which will result in the development of stable prototypes. A complete performance characterization and model development of each technology will be presented.

4: Multiphase, multiscale modelling

Milestone: *Development of a computational model library for multiphase, multiscale models.* The model library will comprise all models of different scale for each of the developed technologies including adsorption/desorption phenomena, kinetics and unit operation models and will be used for scale-up, integration as well as techno-economic analysis. All models will be validated by prototype testing of the new equipment and iteratively refined by more detailed reliable datasets at ideal and spiked process conditions. The fine-tuned final models are used for the evaluation of various process concepts based on the new technologies.

5: Assessment of new technologies in industrial application scenario

Milestone: *Techno-economic analysis and LCA methodology set-up for investigation of INTERACT methodology.* For quantitative decision-making at different stages of the INTERACT project, metrics and tools are used as support in order to provide feedback for technology research to focus on the most promising directions and to decide which technology or which combination of the most promising technologies can be integrated economically and under LCA metric into existing plants. The results will consequently help to guide current as well as future research.

The project was planned for a period of 3.5 years. The members of the consortium were carefully selected to warrant the impact by the participation of highly innovative multinational industrial companies (NZDK/NZNA), research institutions (SINTEF, CID, ICE-PAS, PROD), universities (TUDO, DTU, KULEU) and KMUs (SOLV, SUPREN). The relevant scientific foundations for the development of PIL and enzyme-solvent systems (CID, SOLV, NZDK/NZNA, DTU), the development of gas membranes and membrane contactors (KULEU, SINTEF) and the investigation and characterization of the different technologies (TUDO, DTU, ICE-PAS) were thoroughly covered and aided by the experience in chemical, mechanical and computer aided process engineering (SUPREN).

Description of the main S&T results/foregrounds

WP1: Synthesis and characterization of poly(ionic liquids)

The main objective of WP1 was the development of **tailored poly(ionic liquid)s (PILs)**, which were further applied as active materials in various CO₂ capture technologies. Therefore, the main activities have been focused on the synthesis and characterization of the PILs that represent a subclass of polymers constituted by ionic liquid (IL) monomers (Figure 2). As salts comprised of ions with a wide range of poorly coordinated structures, ILs are liquid below 100°C, or as so-called room temperature ionic liquids (RTIL) even at room temperature. Since ILs show selective affinity towards CO₂ over N₂ or CH₄ due to their polarity, they have been investigated widely in CO₂ capture technologies.² Since ILs are considered expensive and their recovery accordingly important, PILs, which retain the versatility of ILs, but they can be processed as thin films and used as membrane materials in gas separation or as solid sorbents present a huge potential, which is further fostered by their selective, fast and reversible sorption of CO₂.³

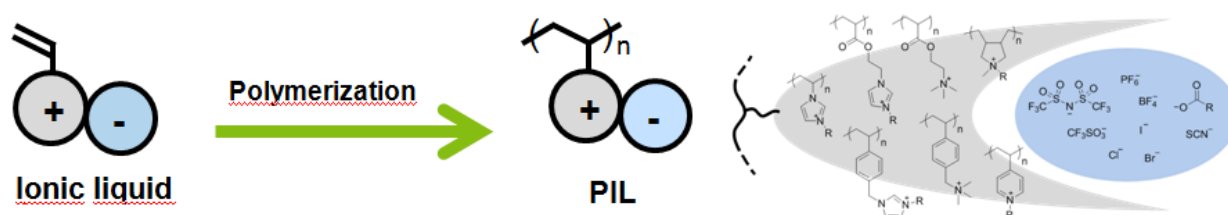


Figure 2: Schematic representation of a poly(ionic liquid).

In the scope of the project, two different types of PILs have been developed. On the one hand, dense (non-porous) PILs have been synthesized and used as active layer in gas separation membranes (WP3) and membrane contactors (WP5), providing a thin dense **semi-permeable barrier** that separates gas components based on differences in solubility and diffusivity. While most of these PILs have been synthesized by polymerization of ionic liquid (IL) monomers and post-functionalization of neutral polymers and electrolytes, others have been formulated as blends comprised of ILs, PILs and additives that were known to increase permeability. On the other hand, porous PILs have been developed and tested as CO₂ sorbents.

Various IL monomers have been taken into account for the different approaches to prepare highly porous and dense PILs. The following types of monomers have been selected for the synthesis:

- Polymerizable ILs (carrying one polymerizable group) for the synthesis of dense PILs: a family of vinylimidazolium based ILs with pending glycol and aliphatic side-chains; methacrylate based ammonium based ILs.
- Cross-linker type ILs (carrying two polymerizable groups) for the synthesis of highly cross-linked porous PILs: imidazolium based dicationic ILs and ammonium based dicationic ILs.
- ILs with a functionalization-site for anchoring to high surface area materials: imidazolium base IL with alkoxysilane pending group.

Porous PILs

Various strategies for the preparation of porous materials (or high surface area materials) were investigated, taking into account hard templating, complexation of PIL/polyelectrolytes,

² L.C. Tome, I.M. Marrucho, Ionic liquid-based materials: a platform to design engineered CO₂ separation membranes, Chemical Society Reviews, 45 (2016) 2785-2824.

³ J.E. Bara, E. Hatakeyama, D.L. Gin, R.D. Noble, Improving CO₂ permeability in polymerized room-temperature ionic liquid gas separation membranes through the formation of a solid composite with a room-temperature ionic liquid, Polymers for Advanced Technologies, 19 (2008) 1415-1420.

functionalization of alumina nanoparticles with ILs, and PIL nanoparticles. Some of the approaches turned out to be time- and energy-consuming and more importantly, difficult to scale up. Looking for a simple, fast, sustainable, and scalable strategy to prepare nanoporous materials based on PILs a new approach has been developed. The synthetic strategy relies on the radical polymerization of crosslinker-type IL monomers in the presence of an analogous IL, which acts as a porogenic solvent (Figure 3).

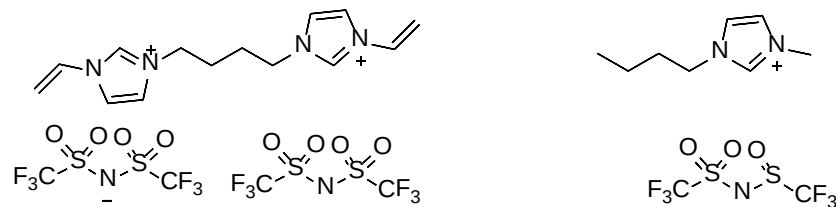


Figure 3: Schematic representation of the synthesis of porous PIL: cross-linker type IL (left) and IL (right).

This IL solvent can be extracted easily after polymerization and recycled for further use. The great advantages of this synthetic approach are the **atom-efficiency and absence of waste**. An illustration of this concept as well as a FSEM image of one of the produced PILs is shown in Figure 4. The effects of different monomer/porogen ratios on the specific surface area, porosity, and pore size have been investigated in the scope of the material development.

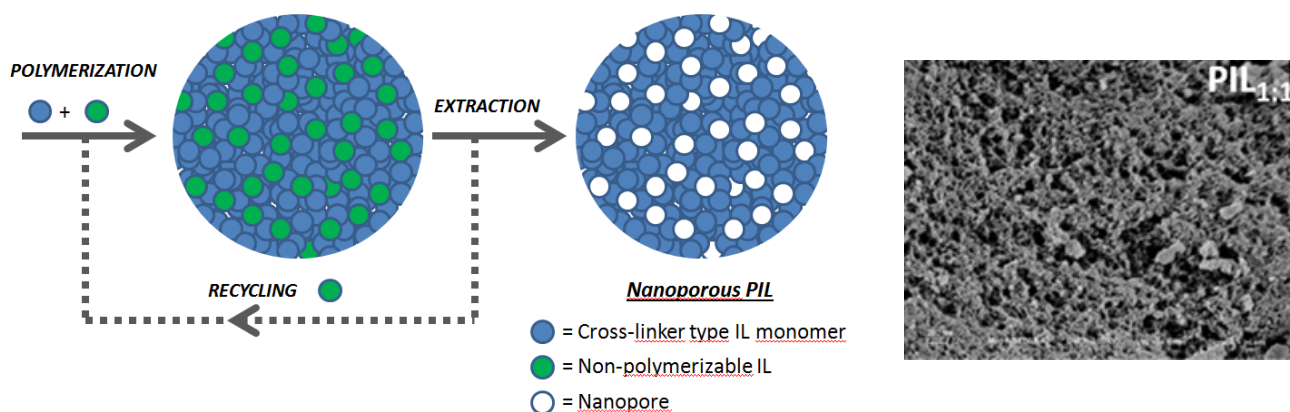


Figure 4: Schematic representation of the synthesis of porous PIL and FESEM photographs of a porous PIL (80 m²/g).

Although the obtained surface area values (up to 80 m²/g) were lower than those reported for materials obtained through the hard-templating pathway, for which specific surface areas of 150-220 m²/g were reported,⁴ the present methodology still remains valuable from the point of view of preparation efficiency and practical convenience. Finally, the potential of the materials as CO₂ sorbents have been evaluated showing competitive performance and enhanced kinetics for the porous materials when compared with other sorbents reported in literature. The sorption capacity of the PILs can further be enhanced by modifying the chemical structure of the IL monomers, selecting cation, anion, and core structure with higher affinity towards CO₂, for example, by increasing the ion polarity.

Dense PILs

Two main strategies to synthesize dense PILs were followed, which are a polymerization of IL monomers and a post-functionalization of existing polymers. The first approach entails the IL being initially synthesized and purified at the monomer level. Homo-polymers and combinations of co-

⁴ A. Wilke, J. Yuan, M. Antonietti, J. Weber, ACS Macro Lett. 2012, 1, 1028 –1031.

polymers can be derived by varying the chemical content of IL monomers. However, the control of molecular weight can turn out to be a major challenge. The post-functionalization on the other hand allows for the conversion of commercial polymers into customized PILs and involves the post-synthetic modifications of neutral polymers through chemical quaternization (e.g. poly(vinylimidazole), poly(vinylbenzyl chloride), poly(diallyl methylamine)) and/or anion exchange reaction, such as poly(diallyldimethylammonium chloride) (P[DADMA][Cl]). During the project different families of PIL have been synthesized and evaluated for gas separation applications, here we present most representative families that have been tested as thin gas separation membranes: PIL/IL/additive blends, PILs derived from commercially available poly(vinylbenzylchloride) and PILs derived from renewable source cellulose.

In the project a new class of composites comprised of **PIL/IL/additive blends** have been prepared and characterized, starting from a commercially available polyelectrolyte through an anion exchange procedure, which is simple and straightforward. The incorporation of the additive to the PIL/IL mixture showed an improvement in both CO₂ solubility and CO₂/N₂ selectivity. CO₂ and N₂ permeation coefficients were determined based on the relevant solubilities and diffusivities as measured gravimetrically at 20°C. Most importantly, it was found that an increase in the additive concentration leads to an increase in the CO₂/N₂ selectivity by a factor of 2.7 (compared with the original PIL/IL material), thus locating the new formulations close to the upper bound on the Robeson plot. A specific formulation, F9:1, showed favourable separation capabilities over a wide pressure range (0 – 18 bar), at temperatures below 40°C. Moreover, composite materials that contain the additives offer CO₂ permeabilities as high as 153 – 428 barrer and CO₂/N₂ selectivities as high as 27 – 82 (depending on temperature and pressure), providing a huge potential for removing CO₂ from flue gas streams. F9:1 also showed the best performance in applications (WP3&5). Another PIL having the same polycation backbone but different anion, a simple carboxylate counterpart, PIL-D-14 is highly hydrophilic and showed higher selectivity ($\alpha_{\text{CO}_2/\text{N}_2}$) but considerably lower permeability, mechanical properties and overall performance.

A direct approach to prepare **PILs** by avoiding the polymerization of IL and the related inconveniences, such as molecular weight control, is **the functionalization of neutral polymers**. A wide range of commercial polymers can be derivatized into PILs. In the INTERACT project, the well available poly(vinylbenzylchloride) has been selected as starting material due to several advantages, having the poly(styrene) backbone, which enhances the CO₂ separation performance in comparison with other PILs based on the CO₂ and N₂ sorption capacities⁵, as the basis of material synthetic procedures, as well as a reactive site to react with amines to create ionic moieties. Three different poly(vinylbenzylchloride) analogues were prepared with IL-sites. An ammonium-derivatised polymer-analogue was prepared as a first PIL-type by polymerisation of an IL monomer, whereas two other PILs were synthesized from poly(vinylbenzylchloride) using a tertiary amine with a pending hydroxyl group and a cyclic tertiary amine. Introduction of fluorinated anions was accomplished by anion metathesis. A thorough characterisation of the material structure, composition, membrane morphology and gas separation properties analyzed in WP3 showed that that mixed-gas selectivity increases with the larger positive charge density of the cation species and that the presence of hydroxyl groups in the polycation enhanced the interaction with CO₂ molecules. In general, the separation performance of the polymeric membranes is significantly affected by the process conditions, e.g. presence of water vapour in the feed stream. As a matter of fact, the experiments performed in humidified conditions revealed a doubled CO₂ permeability in comparison to dry conditions.

Another material that was investigated for PIL synthesis is cellulose, which is not only one of the most abundant and sustainable resources available, but cellulose acetate (CA) membranes are already

⁵ J. Tang, H. Tang, W. Sun, H. Plancher, M. Radosz and Y. Shen, in Chem. Commun., 2005, 26, 3325-3327.

commercially used for large scale CO₂ separation, such as natural gas sweetening. Nevertheless, the development of novel materials in the scope of the industrial use of cellulose and its derivatives is an active field of research (Figure 5). There are promising attempts showing that the functionalization of polymers, such as polybenzimidazoles, with ionic moieties leads to favourable synergies for CO₂ separation. Hence, the synthesis and characterization of a **novel cellulose derived PIL family** as a CO₂ separation membrane material was investigated in detail.

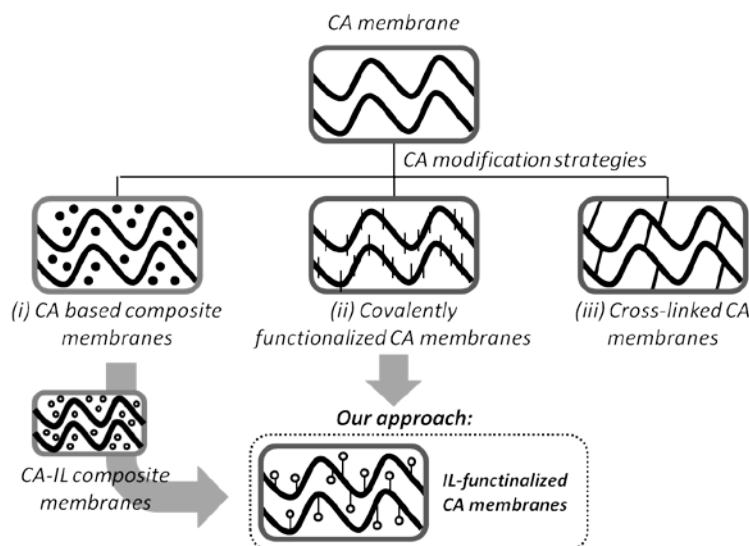


Figure 5: Schematic representation of various CA modified membranes.

The cellulose acetate derived PIL showed interesting preliminary gas separation properties (two-fold increased permeability compared to cellulose acetate) and features several advantages compared to other cellulose acetate derived materials that combine ionic liquids. Building on the synthesis that starts with the post-functionalization of a renewable, cheap and well-known industrial raw material (cellulose acetate) that comes without the need of controlled polymerization reactions the ionic groups are covalently grafted to the polymer matrix. In order to further investigate the potential of this material a family of related PILs was developed by changing the nature of the pending cations and incorporating chemical bonds that enable cross-linking. The effect of the cationic moiety chemical structure on the CO₂ sorption capacity was investigated in gravimetric experiments and as TFC membranes for CO₂ removal from flue gas (WP3). Those materials showed selectivities comparable to first PIL with stable CO₂ permeabilities over the range of CO₂ partial pressures in the experiments with different volumetric composition of feed gas and different applied pressures).

Improved synthetic strategies for economic, scalable and feasible industrial production of functionalized PILs

Throughout the project the selection of IL monomer and PILs was performed by carefully designing reaction pathways in view of using non-toxic and industrially available raw materials as far as possible (REACH, CMR products, safety issues are taken into account) and in consideration of a necessary scale-up of the production process. For the demonstration of the upscaling potential, the production of poly(diallyldimethyl ammonium) bis(trifluoromethanesulfonyl)imide), one of the promising PILs, was scaled up from 100 g batches up to 1kg batches. While bigger reactor sizes were not found to be efficient in reproducing the same quality than lab scale, the amount of PIL is sufficient for large-scale gas membrane applications, taking into account that only the active layer of the membrane has to be produced from the PIL. By taking into account **new mixers and equipment options** the scale-up was successfully performed and commercialization of this PIL has started. The developed equipment is flexible enough, such that other powders and additives can be scaled up, as

well. Further improvement of the synthetic strategies for economic, scalable and feasible industrial production of functionalized PILs was carried out through a 1kg and 100kg production simulation for ten compounds.

Mathematical description of sorption/desorption phenomena of main components of flue gases on mesoporous PILs

A mathematical description of sorption/desorption phenomena of main components of flue gases on mesoporous PILs and its validation against experimental data concerning carbon dioxide sorption on the first set of mesoporous PILs has been carried out. The dual-mode model was developed which is widely used to describe gas solubility and transport in glassy polymers and applied also in the case of CO₂ and other gases sorption into PILs. The model adopts the concept of sorption into two idealized environments: dissolved and “microvoids” explaining in that way a non-linearity observed in sorption isotherms of gases on PILs. The sorption in a dissolved environment is described by Henry’s law relation and the sorption in the “microvoids” is described as the Langmuir adsorption or “hole-filling” process. Apart from dual-mode model describing sorption equilibria the linear-driving force model was also applied in order to determine diffusivities from uptake curves accompanying each experimental point of sorption isotherms. The **dual-mode model** was validated against experimental data of CO₂ sorption on first sets on mesoporous PILs based on imidazolium bis(trifluorosulfonyl)imide and ammonium bis(trifluorosulfonyl)imide and prepared using different monomer-to-porogen ratios. Coefficients of the dual-mode equation were determined and it was shown that the model describes experimental data with a very good accuracy. The physical meaning of the coefficients was also discussed as well as their usefulness in determining some other important parameters such as heat of sorption.

WP2: Characterization and functionalization of enzymes

The main focus of WP2 was on the development and characterization of enzyme-solvent systems for the implementation in enzymatically enhanced reactive absorption processes. A selection process was established to determine technological applications where rate enhancement can be practically and economically exploited by screening combinations of suitable enzyme-solvent systems, evaluating options for retaining/recycling the enzymes, and characterizing enzyme stability and kinetic performance under operating conditions.

Enzyme stability

Being considered as a major issue for the application of enzymes in industrial environments, the first investigations focussed on the investigation of enzyme stability, which depends on pH, temperature and the selected solvent system. Since the temperature of the solvent changes while passing through the different process units, the highest temperatures are encountered in the stripper, which in conventional CO₂ absorption processes is operated well above 100 °C. In addition to temperature the pH of the solvent system changes as well, depending on the CO₂ loading. Since CO₂ is acidic, the highest pH is encountered at the lean loading of the solvent, after leaving the stripper and prior to entering the absorption (Figure 6).

The main results from the investigation of the performed **enzyme stability** tests are summarized in Figure 7 and Table 1, which illustrate the dependence of enzyme stability on pH and temperature, as well as the results from long-term stability trials for various investigated enzyme-solvent systems. It can be concluded that the enzyme retains more than 90% of its initial activity when operating conditions are confined to a range of pH between 7 and 11.

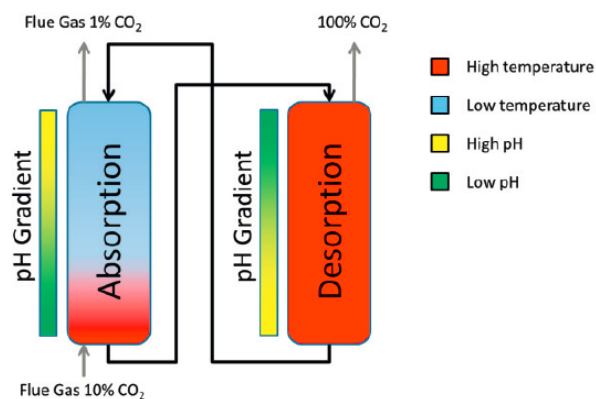


Figure 6: Illustration of temperature and pH gradient over the course of an absorption/desorption cycle.⁶

Full retention of enzyme stability was experienced at temperatures up to 50°C, while minor deactivation up to a 75% activity resulted from a temperature increase to 60 °C. At higher temperatures the residual enzyme activity was dropping below the level of detection within a timeframe of 100hrs. Consequently high activity of the enzymes can be maintained when process conditions are confined to the determined stability ranges.

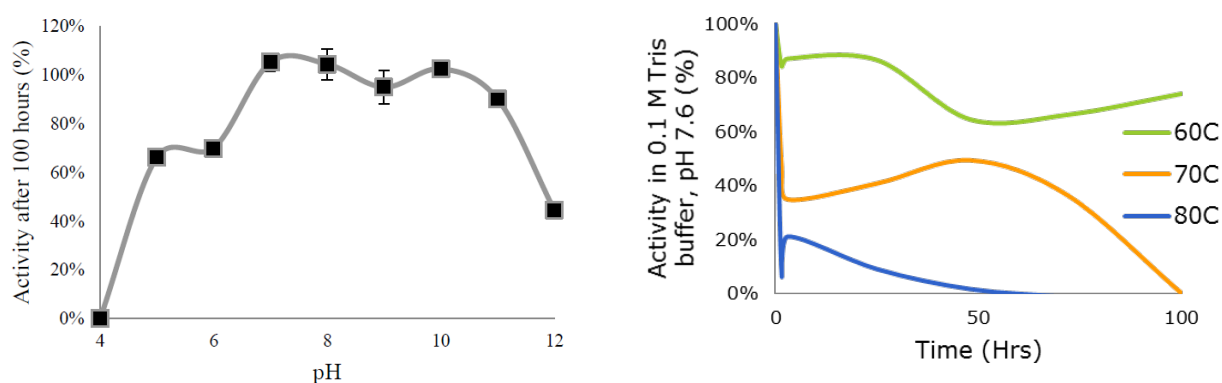


Figure 7: pH and temperature stability of CA.

The results of a long-term investigation (150 days) of six promising aqueous solvents (Monoethanolamine (MEA), 2-Amino-2-methyl-1-propanol (AMP), N-Methyldiethanolamine (MDEA), 2-aminoisobutyric acid (AIB), Potassium carbonate (K₂CO₃), and chlorideAmmonium chloride (AC) and the solvent 3-(methylamino)propylamine (MAPA) used together with MDEA as a mixed solvent) are presented in Tble 1. These solvents were chosen due to their reported positive results for CCS application. All solvents otherthan K₂CO₃ were used with a 3M concentration, wheras K₂CO₃ was applied at lower concentration due to solubility problems due to which the enzyme precipitated with the solvent resulting in a drastically reduced enzyme activity. Equal solvent concentrations were chosen to give a fair comparison based on the fact that CO₂ is absorbed with a 1:1 ratio with these solvents. It should be noted that due to a different reaction mechanism, MEA absorbs 50% less CO₂ per mol, than the other solvents. The pH's used is the, investigating enzyme stability in the pH ranges between 8-10. The lowest pH represents the fully loaded solvent. The combined effect of temperature, solvent concentration and solvent type was tested.

⁶ Gundersen, M. T.; von Solms, N.; Woodley, J. M. Energy Procedia 2014, 63, 624–632.

It can be concluded that within the defined operating conditions the resulting enzyme stability shows great promise towards implementation, justifying the further investigations in WP4 and WP5 for application in columns and membrane contactors.

Table 1: Stability with different solvents after 5 and 150 days⁷

Solvent (concentration)	pH	Residual Activity 5 days (%)	Residual Activity 150 days (%)
MEA (3M)	8.3	95 ± 0.4	73 ± 1 0.8
	10	76 ± 1.8	33 ± 4.8
AMP (3M)	9	99 ± 0.3	42 ± 1.6
	10	104 ± 7.7	12 ± 0.6
MDEA (3M)	9	92 ± 2.8	62 ± 4.0
	10	91 ± 3.0	54 ± 2.5
AIB (3M)	8	106 ± 4.9	91 ± 3.0
	10	95 ± 0.1	35 ± 0.9
K ₂ CO ₃ (1M)	8	116 ± 6.8	83 ± 3.6
	10	85 ± 1.2	29 ± 2.4
MAPA (1M)/ MDEA (2M)	8.6	86 ± 10.3	85 ± 0.5
	10	99 ± 4.8	69 ± 4.4
AC (3M)	8	99 ± 4.8	71 ± 5.1
	10	100 ± 4.7	22 ± 3.4

Enzyme kinetics

While sufficient enzyme stability is a prerequisite for the application in an industrial environment the enzyme needs to add sufficient benefit to the process to justify the limited operating range. In order to quantify and model the obtainable benefit from enzyme application, the **mass transfer** of CO₂ in different solvents was measured in a wetted wall column and the kinetics of the enzyme in the solution were determined taking into account the well-defined interfacial area in the experimental equipment. Based on the previous screening of enzyme-solvent systems the primary amine MEA, the tertiary amine MDEA and the sterically hindered amine AMP were investigated in aqueous solutions with 30 wt% solvent, while due to limited solubility the carbonate salt K₂CO₃ was investigated in an aqueous solution with 15 wt% solvent.

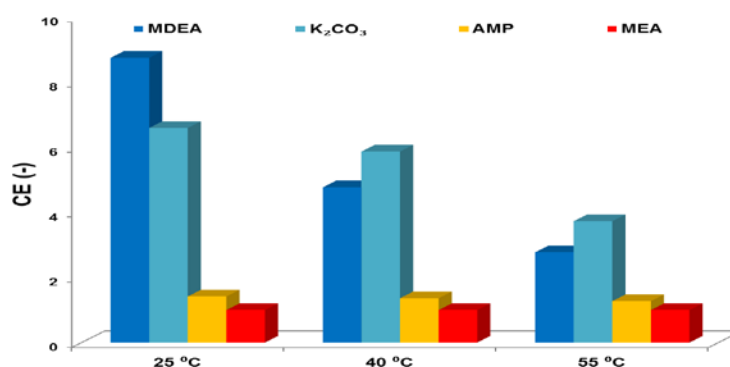


Figure 8: Mass transfer enhancement due to 2 g/L CA addition

⁷ Gundersen, M. T.; von Solms, N.; Woodley, J. M. Energy Procedia 2014, 63, 624–632.

CO₂ mass transfer was quantified for the solvents with and without the addition of 2 g/L CA. In order to quantify the benefit of the enzyme addition the so-called catalytic effect (CE), which represents the ratio of the measured CO₂ transfer with and without the added enzyme, has been determined for each enzyme-solvent system. The results are summarized in Figure 8. Obviously a significant **enhancement of the mass transfer** can be achieved by enzyme addition in the MDEA and K₂CO₃ solvent systems, whilst the improvement in AMP and MEA solvent systems is small or negligible under the conditions of these tests.

Based on the promising results achieved (including the stability results) and beneficial thermodynamic properties (i.e. high equilibrium CO₂ loading), the solvent MDEA was chosen to be further investigated in packed columns at pilot scale in WP4. Building up on continuous experiments a mechanistic enzyme kinetic model was derived, based on a simplified Michaelis Menten type kinetic with product inhibition by the bicarbonate ion for CA, which can efficiently describe the effect of temperature, solvent concentration, enzyme concentration and solvent loading on the mass transfer. The quality of the derived model is illustrated by comparison to experimental results in Figure 9. This derived kinetic model was further implemented in a rate-based absorber column model in WP4.

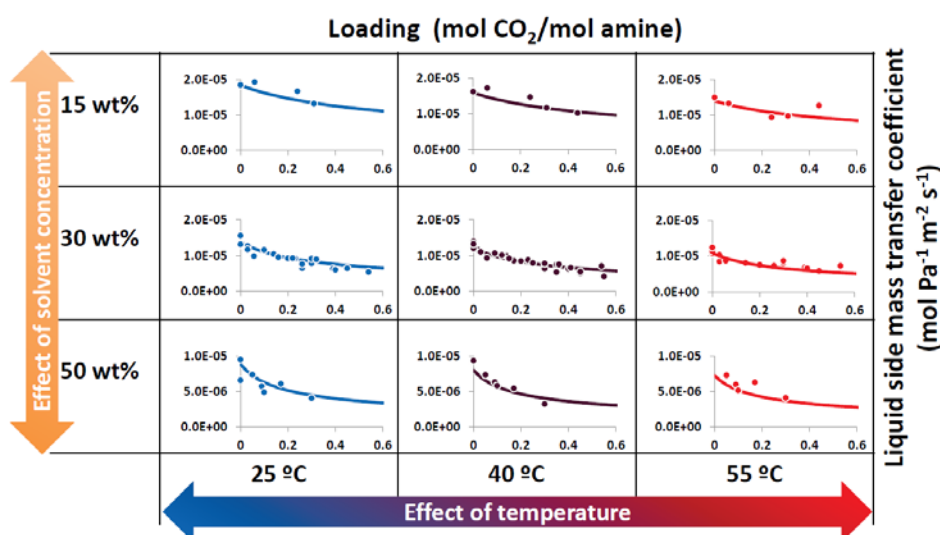


Figure 9: Model for the liquid side mass transfer coefficient of enzyme enhanced MDEA

Enzyme immobilization

In order to protect the enzyme from the harsh conditions, especially in terms of temperature, that are usually experienced in the stripper, different concepts for immobilization of the enzyme in the absorption step were investigated. Free enzymes in solution either as soluble enzymes or immobilized on particles distributed in the solvent, will experience a variety of conditions throughout the process. Effective immobilization can provide increased stability of the enzyme by restraining the enzyme to preferred ranges of pH and temperature corresponding to the operating conditions of the absorber, resulting in increased lifetime of the enzyme. However, immobilization adds cost in developing the formula and producing the immobilized form of enzyme, and can cause additional mass transfer limitations. Finally, replenishing immobilized enzyme might introduce additional complexity in a capture process and require appropriate scheduling.

The first investigated immobilization strategy was a surface coating of an enzyme polymer mixture on the structured packing. Due to insufficient compatibility of the enzyme CA with the coating material this strategy was however not successful. Furthermore, another concept that was investigated was the immobilization of enzymes on magnetic nanoparticles, however this option was also discarded after initial experiments. A third concept the immobilization of enzymes on silica granules via spray coating, forming so-called enzyme beads, which can be filled into pockets of specific catalytic structured packings, such as Sulzer Katapak SP, presented a very promising and well working solution. Stability investigations for the immobilized enzyme were performed with a specially constructed test rig, in order to evaluate the mechanical stability of the particles as well as stability of the enzyme immobilization on the particle. These investigations were performed in a glass column equipped with catalytic packing operated in a closed loop setup with a constant solvent flow supplied to the top of the column, while counter-currently contacted with a CO₂ containing gas stream and an aqueous K₂CO₃ solvent at temperatures between 20-40°C. Consequently, the particles experience comparable mechanical and chemical stress as in a later investigated pilot plant application. The total washout did not exceed 15 wt%, whereas no further washout was observed after a period of 8hrs. The application of this form of immobilization can therefore be recommended from the perspective of applicability and stability of the enzyme beads concerning mechanical and chemical stress. Nevertheless, a novel form of immobilized CA became available for testing through the strong extended network of INTERACT partners at the end of the project which provided even bigger prospect. This material, tested at the end of WP4, showed significant promise as a new way to provide highly active CA to the system for good absorption performance over long time periods (see WP4 for further information).

Enzyme recovery– modelling

Finally, the use of an additional separation step to recover dissolved enzyme prior to entering the stripper was modelled based on calculations adding an ultrafiltration (UF) membrane and investigating the effect of different enzyme recoveries at various operating temperatures for the stripper. A theoretical investigation was performed, using experimentally determined enzyme deactivation rates from INTERACT, which were modelled by a first order reaction rate. The results of this study are exemplarily illustrated in Figure 10, showing that fast deactivation of the enzyme is expected at stripper temperatures above 70°C, requiring frequent exchange of the enzyme solvent-system unless the enzyme is immobilized or recovered by an additional UF separation.

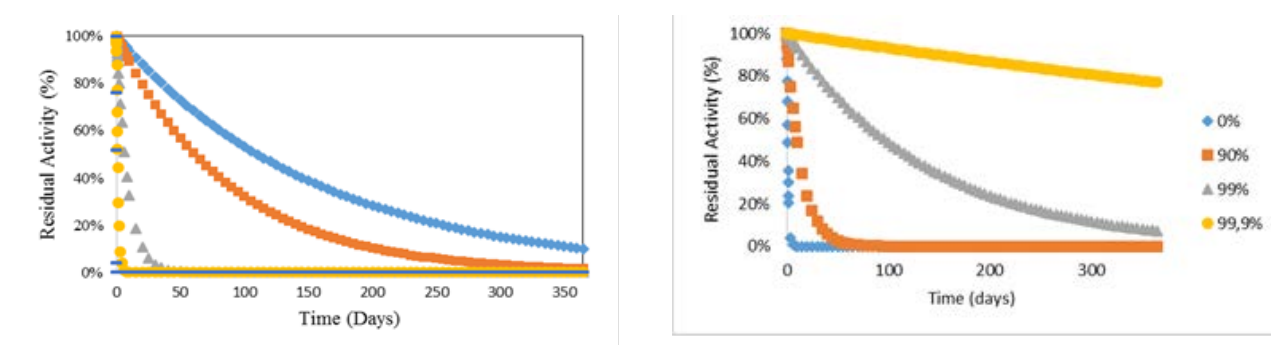


Figure 10: Residual enzyme activity after one year of operation without enzyme recovery by a UF membrane at stripper temperatures of 60 °C (blue diamond), 70 °C (Orange squares), 80 °C (grey triangles), 90 °C (yellow circles) and 100 °C (blue dashes) [left] as well residual enzyme activity after one year of operation with enzyme recovery by a UF membrane

at a stripper temperature of 90°C, assuming enzyme recovery of 90% (orange squares), 99% (grey triangles) and 99.9% (yellow circles)⁸. Application without a UF membrane is shown as reference (blue diamond).

WP3: Gas separation membranes

The major objective of WP3 was to implement the dense PILs developed in WP1 as the selective layer of thin-film composite (TFC) membranes for the separation of CO₂ from flue gas streams. An illustration of the concept is given in Figure 11. The PIL was applied as a film with a micrometre thickness on a porous support that provided mechanical resistance to the applied pressure difference. Different TFC membranes were developed using either in-house prepared or commercially available polymeric supports. Various factors were taken into account when selecting appropriate support materials, seeking negligible surface roughness to allow the formation of defect free PIL layer, and stability in the desired solvents during casting to avoid disintegration of the membrane morphology. Besides the separation performance of the selective PIL, physical and mechanical parameters of the layer were considered in terms of film-forming properties and integral stability.

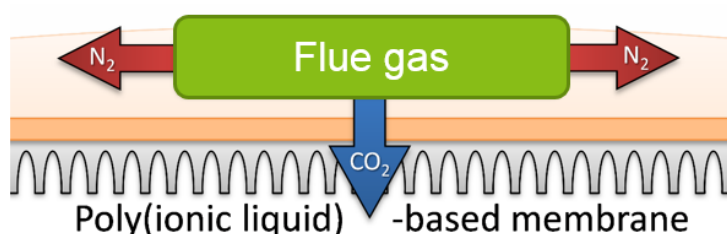


Figure 11: Concept of PIL based composite membrane for CO₂ separation from flue gas.

For an initial investigation of the separation properties, the flat-sheet membrane geometry was considered as most suitable, as it also enables simplified membrane fabrication via physical layer deposition techniques, such as solvent casting and spray coating of the PIL directly on to the support. This efficient method for preparation and investigation of TFC membranes was used to determine the optimal selective layer materials with good characteristics both in terms of the physical processing (i.e. film formation, synthesis scale-up, expenses) and CO₂ separation performance (i.e. permeability, and selectivity). A synthetic flue gas stream with a CO₂/N₂ molar ratio of 15/85, 1.2 bar feed pressure and a process temperature of 26 °C has been chosen for the investigation of separation performance. The acquired data on membrane separation performance was further processed to derive and verify mathematical models for the gas permeation membranes. The most promising samples were finally tested under pre-defined real gas conditions, taking into account a humidified gas with realistic temperature, CO₂ concentration, and traces of SO₂ and O₂ as would be expected in the flue gas of a coal fired power plant.

Development of the membrane prototype

Different membrane prototypes were prepared by application of active membrane layers consisting of PIL materials developed by CIDETEC and SOLVIONIC. While an extensive investigation of commercially available supports was conducted at SINTEF, lab made polymer supports that showed sufficient resistance towards solvent swelling, were considered at KU Leuven. In selecting commercially available supports the focus was placed on slightly hydrophobic supports in order to prevent pore penetration of the hydrophilic PILs inside the support. Pore penetration decreases the gas permeance and simultaneously may result in defects in the coating layer, which significantly reduced CO₂/N₂ selectivity. The selection of supports further addressed stability, ease of handling,

⁸ Gundersen, M. T.; Gladis, A.; Loldrup Fosbøl, P.; von Solms, N.; Woodley, J. M. Energy Procedia 2017.

cost, reduced surface roughness and good wettability. Membranes of various PIL materials were successfully fabricated using casting and ultrasonic spray coating procedures forming continuous films in the range of 0.5 – 20 μm thickness. The fabrication of TFC membranes using ultrasonic spray coating procedures to disperse the selective PIL layer on the membrane support is a relatively new concept with few reports of this in the literature. It is also a scalable technique and interesting from an manufacturing standpoint.

Screening in lab-scale experiments under dry and humid conditions

Mixed-gas selectivities and CO_2 permeance were measured during permeation experiments with a gaseous mixture of 15% CO_2 in N_2 for PIL-based TFC membranes mounted in a custom-built high-throughput gas separation (HTGS) flat sheet membrane module at KU Leuven. The HTGS setup is shown in Figure 12. The screening was carried out in dry conditions with up to 5 bar feed pressure to facilitate the gas transfer across the separation barrier.

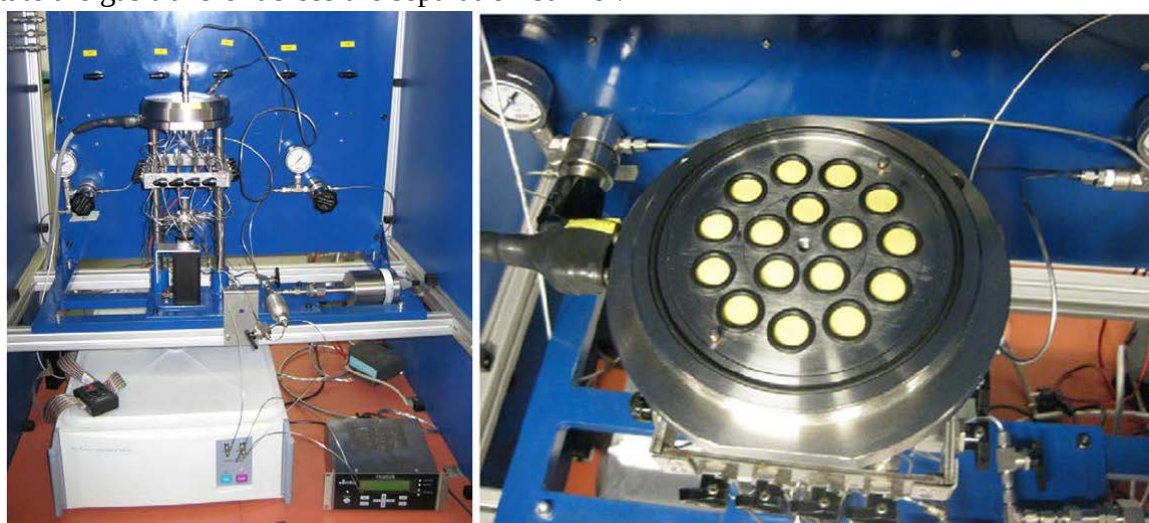


Figure 12: Overview of the HTGS set-up with compact GC (left) and detail of the 16 position membrane module (right).

Furthermore, permeation tests were performed in a custom designed test rig at SINTEF, using similar conditions to real flue gas conditions (15% CO_2 in N_2 , 90% humidity). Although different membranes (different supports and membrane thickness as result of different preparation procedures) were tested, it became evident that compared with dry gas experiments the humidified conditions influence the membrane separation performance. The key figures from two of the most promising membrane materials PIL_D_14, giving high selectivity, and F9:1, giving high permeability, as well as high selectivity, are highlighted in Table 2 below. The data sets comprise performance characteristics for both dry gas measurements, and humidified gas. While the selectivity of the membranes prepared with F9:1 seems independent of humidity and membrane thickness, there seems to be an increase (about a factor 2) in permeability at humidified conditions. For PIL_D_14 membranes on the other hand, humidified conditions seem to affect both the selectivity and permeability.

Table 2: Performance characteristics for the most promising PILs chosen for further investigations

PIL	Partner	δ^a	$\alpha_{\text{CO}_2/\text{N}_2}^b$	$P_{\text{CO}_2}^c$	Permeance ^d
		[μm]	[-]	[Barrer]	[$\text{m}^3(\text{STP})/\text{m}^2 \text{ bar h}$]
F9:1	KULEU	1.8	34	217	0.333

	SINTEF	11.7	33	464	0.0130
PIL_D_14	KULEU	1.7	24	8	0.0130
	SINTEF	2.0	58	247	0.034

(a = Thickness of the active layer, b = Mixed-gas selectivity, c = Permeability of carbon dioxide, d = Permeance of carbon dioxide)

Mathematical model of the gas permeation through the membrane under spiked process conditions

In order to evaluate the potential of the PIL-based gas membranes and develop suitable process design configurations in WP 6&7, a mathematical model of a gas membrane module was developed in gPROMS. The model allows for the consideration of various flow patterns of feed gas and permeate, as well as the evaluation of applied vacuum and sweep gas for generation of a suitable driving force for mass transfer and produces two streams, a purified gas (retentate) and a permeate stream (CO₂-rich gas). The membrane model performance has been assessed using spiked gas conditions, taking into account a fed gas mixture consisting of CO₂, O₂ and N₂ (with or without the presence of water vapour) whose composition and flow rate reflects those of the real reference flue gas. For a single membrane module with PIL (SOLVIONIC F9:1) active layer a single stage as well as multi-stage configurations were investigated, taking into account the separation of a 3-components CO₂/O₂/N₂ mixture as dry gas and in the presence of water vapour. While for the first case permeability coefficients were determined from pure and dry gas experiments they were based on permeation tests using spiked conditions (15 % CO₂ in N₂, 90 % humidity) for the other cases. A permeate pressure of 0.25 bar was assumed for all these cases, while membrane area and feed gas pressure were varied in form of a sensitivity study.

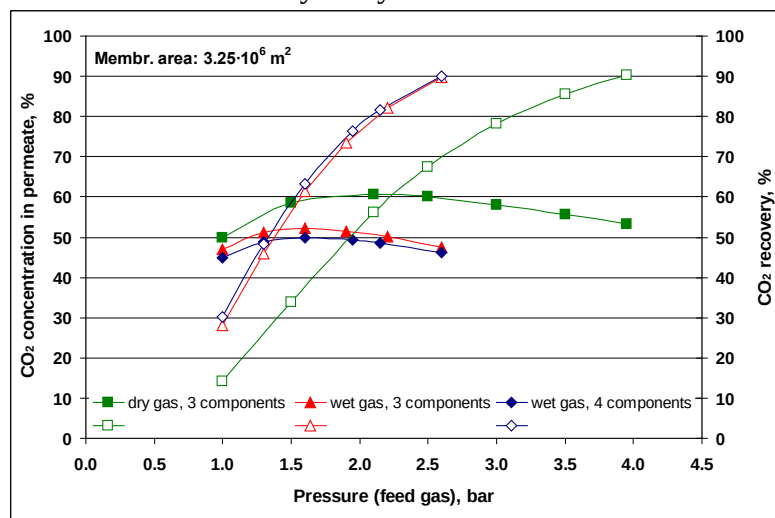


Figure 13: CO₂ enrichment and recovery vs. feed gas pressure for the membrane area of 3.25x10⁶ m². Solid symbols denote concentration and empty symbols denote recovery.

As a result, maps of CO₂ purity, recovery and feed pressure were determined based on the simulation results for a given membrane area. An exemplary result of these calculations is given in Figure 13. From the results it can be concluded that the presence of H₂O in the feed mixture reduces the CO₂ concentration in the permeate, whereas it has a strong beneficial effect on CO₂ recovery.

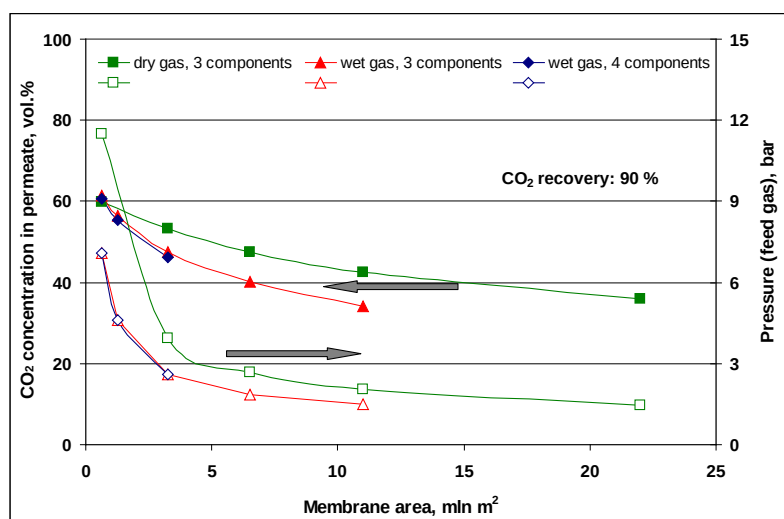


Figure 14: Simulation cases with CO₂ recovery of 90%. Solid symbols denote concentration and empty symbols denote recovery.

Based on the relationship between CO₂ purity, recovery, membrane area and feed pressure, determined in simulations, cases with CO₂ recovery of 90 % were selected (see Figure 14). It can be concluded that the considered membrane can provide 90 % CO₂ recovery in a permeate stream containing 36-60 vol% of CO₂ (dry gas) and 34-61 vol% of CO₂ (wet gas).

Performance under realistic flue gas conditions

In order to validate the obtained results for membrane performance obtained for idealized conditions and to verify the stability of the developed membrane materials further experimental investigations were performed under real process conditions. The most promising PIL (F9:1) developed by Solvionic was used as the selective material for membranes that were successfully prepared using ultrasonic spray coating, forming continuous films in the range of 5– 20 µm thickness on commercial polysulfone or lab-made polyimide support. Other membranes based on the materials from the same PIL family were further investigated as well and compared with PIL (F9:1). The influence of the process operation conditions was compared for vacuum and sweep gas driven mode in the experiments with dry gas. The results revealed that permeance was at least one order of magnitude higher in the vacuum driven process, while the selectivities were higher in the sweep gas driven mode. It was further observed that humidity positively affects the permeance of the membranes containing ionic liquids and salt additive. However, only small improvement in the CO₂ selectivity could be achieved. The durability of the F9:1 membrane material upon exposure to a synthetic flue gas containing 15% CO₂ and contaminating components, such as O₂ and SO₂ in humidified conditions, was investigated over 1500 h with 5% O₂, including 500 h with 300 ppm SO₂. There was no negative impact from these components on the membrane performance over this extended timeframe. Subsequently, long-term temperature stability was investigated up to an operating temperature of 75 °C. An increase of CO₂ flux and decrease of CO₂/N₂ selectivity with increasing temperature was observed. The results from dry gas measurements, realistic gas measurements as well as durability tests, enabled to define a robust dataset for the performance characteristics including process and equipment parameters, as well as operating windows for the F9:1-based membranes.

WP4: Absorption in columns

Building up on the results obtained in WP2 the identified enzyme-solvent systems as well as developed immobilization strategies were further applied to packed columns for the investigation of

their performance in reactive absorption of CO_2 in WP4. While enzyme stability and rate improvements due to the presence of the biocatalyst are prerequisites for a feasible application it is important to evaluate the optimal choice of enzyme-solvent system and operating conditions in order to exploit the potential benefits and outperform currently applied solvent systems.

Experimental investigations of absorption with enzyme accelerated solvents

An illustration of the significant catalytic effects for these solvent systems was already presented in the context of WP2 in Figure 8. In general it can be concluded from the different solvent systems, which differ in the underlying reaction mechanism with CO_2 , that all solvents that form bicarbonate (all but MEA) showed a positive effect of CA addition on mass transfer. The catalytic effect of the enzyme, which is defined as ratio of the absorption rates between blank and enzyme accelerated solvents, showed a declining trend at higher temperatures. Experiments at different solvent concentrations revealed that higher MDEA and K_2CO_3 concentrations gave lower relative mass transfer rates benefits for the enzyme-solvent systems compared to solvent without enzyme. The optimum process conditions for high mass transfer in enzyme enhanced aqueous MDEA solutions were consequently identified to be low absorption temperature and low solvent concentration.

The most promising enzyme-solvent systems, which are based on aqueous solutions of K_2CO_3 and MDEA, were further investigated in technical scale absorption columns. At TUDO an absorption column with DN50 and a packing height of 2.3 m was equipped with Sulzer BX structured packing for the investigation of enzyme-solvent systems with dissolved enzyme. Comparable experiments showing the same trends and validating the obtained results were conducted in the technical scale absorber at DTU, which had a packing height of 8.2 m (filled with Sulzer Mellapak 250 Y) and a diameter of 0.1 m. Both experimental setups are presented in Figure 15.



Figure 15: Experimental setups of DTU (left) and TUDO (right)

Operating the column at a gas load of $0.93 \text{ Pa}^{0.5}$ and three different liquid loads between 8 and $24 \text{ m}^3 \text{ m}^{-2} \text{ h}^{-1}$, the performance of the enzyme-solvent systems was first tested at common operating temperatures of 40°C , referring to the temperature of the entering solvent.

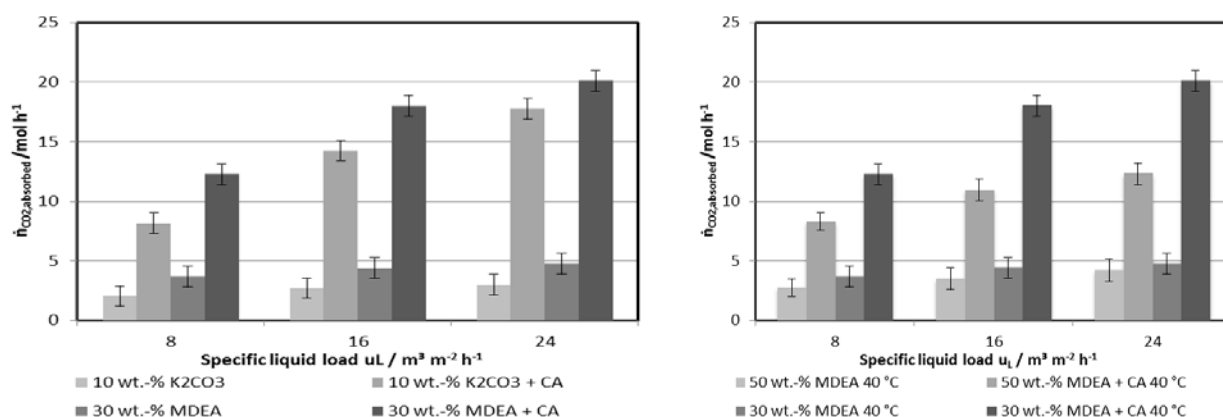


Figure 16: Absorbed mole flow of CO_2 in technical scale absorber column for most promising solvents (left) and influence of MDEA concentration on absorbed mole flow of CO_2 (right) at 40°C solvent inlet temperature.

Each aqueous solvent system was investigated without and with addition of 0.2 wt.-% of CA for a synthetic flue gas with a CO_2 volume fraction of 15 vol.-%. From analysis of the CO_2 content in the gas inlet and outlet with NDIR sensors the absorbed mole flow of CO_2 was determined and compared as illustrated in Figure 16 (left). The results indicate that the previously determined catalytic effects can be obtained at higher liquid loads and that as indicated by the lab-scale experiments the MDEA-based solvent system outperforms the K_2CO_3 -based solvent system in terms of absorbed mole flow rates. Furthermore, operational issues with K_2CO_3 occurred during the experiments because the enzyme was precipitating in the K_2CO_3 solution. Consequently, MDEA was selected as most promising solvent for more detailed studies in technical scale. In these studies the solvent concentration was increased to 50 wt.-% in order to investigate the effect of varying the composition of the solvent system. The results, which are illustrated in 16 (right), indicate that the increased amine concentration causes a reduction in absorbed mole flow and therefore 30wt% MDEA solutions or even lower chemical concentrations are to be preferred. This result is in good agreement with the previous observation of the importance of the bicarbonate formation for the rate enhancement by addition of the enzyme.

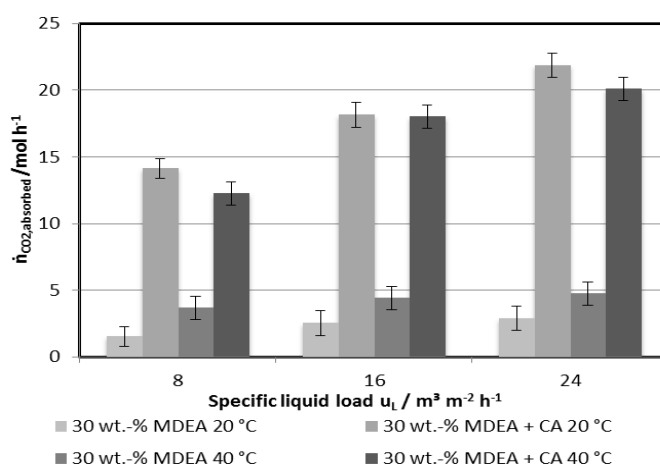


Figure 17: Influence of solvent inlet temperature of the absorber column on absorbed mole flow of CO_2

Furthermore, the liquid inlet temperature was reduced from 40 °C to 20 °C, which for chemical reactive absorption is usually resulting in a reduction in reaction rates because of an Arrhenius-like dependence of the reaction rate constants from temperature. The results of this investigation, which are illustrated in Figure 17, indicate however that the decreased liquid inlet temperature has no significant influence on the absorbed mole flow for the enzyme-solvent system. This unique feature offers a significant potential for enzyme accelerated solvents, since at lower temperatures higher CO₂ loadings can be achieved, which enable operation at higher cyclic loads and therefore reduced solvent flow rates. Accordingly, an aqueous MDEA solution with MDEA concentration of 30 wt.-% that provides good CO₂ loading capacity and a liquid inlet temperature as low as technically feasible (most likely 25 °C) is recommended as promising for further evaluation.

For this the performance of the enzyme enhanced solvent system was further benchmarked against the proven state-of-the art solvent system, taking into account a 30 wt.-% MEA solution and comparing the performance under similar conditions as the enzyme enhanced MDEA solvent. To highlight the comparability of the kinetic performance and the improvement by the addition of the enzyme the absorption rates for different solvents were evaluated in the 10m column at DTU. The results, which are indicated in Figure 18 (left), indicate the significantly increased absorption rates of the 30wt% MDEA solution by addition of 0.9 g/L CA and 3.5 g/L CA, as well as the improvement of mass transfer with increased liquid load. Furthermore, a direct comparison with the industrial standard 30 wt.-% MEA solution in 18 (right), highlights that without the enzyme the aqueous MDEA solution reaches only 20 % of the absorbed mole flow measured for a 30 wt.-% MEA solution. Addition of the enzyme improves the performance to 40-58 % and 68-76 % of the absorbed mole flow measured for a 30 wt.-% MEA solution for an enzyme concentration of 0.9 g/L CA and 3.5 g/L respectively.

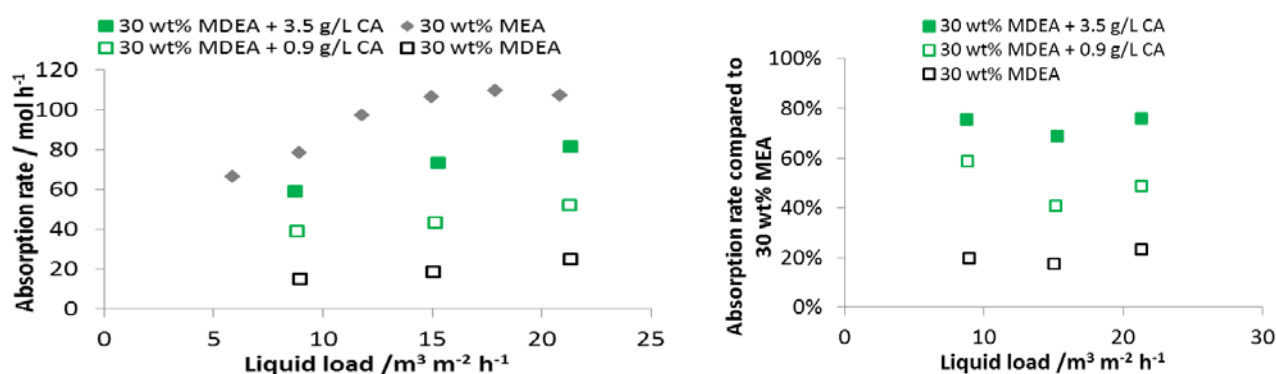


Figure 18: Experimental results of the influence of liquid load on the total absorbed mol flow of CO₂ at 10m column height and 28 °C inlet temperature (left) and relation to the 30wt% MEA solution (right)

Immobilized enzymes

In addition to the application of dissolved enzyme, different immobilization strategies for enzyme application were considered in WP2&4. The immobilization of enzyme beads in the bags of the catalytic packing Sulzer Katapak SP, which was considered as most suitable option in WP2, was successfully implemented in the technical scale absorber at TUDO. However, the enhancement of the absorbed mole flow of CO₂ was not as significant as for the dissolved enzyme, which was mainly explained by the significantly lower concentration of enzyme that was approximately a factor of 50 smaller compared to the 0.2 wt.-% CA applied in the solution. Taking into account that the technical feasibility of this concept was proven, further improvements in the production of the enzyme beads

would be likely to increase the enzyme accessibility significantly and this aspect is recommended for future development.

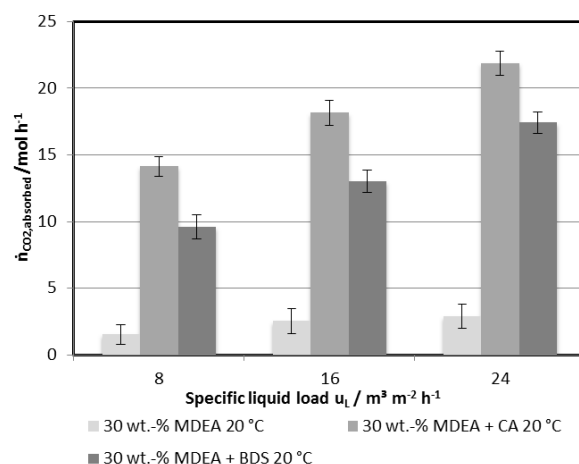


Figure 19: Influence of BDS on absorbed mole flow of CO₂

Finally a new and highly innovative immobilization concept that was not considered in WP2 was investigated, the so-called biocatalyst delivery system (BDS), initially developed by Akermis Inc.⁹. In this concept the enzyme is encapsulated by polymeric microparticles, which can be fully mixed with the solvent when properly agitated, while the lower density and hydrophobicity of the material allows them to float on the solvent as soon as agitation is stopped. Therefore, the BDS can be applied as homogeneous solvent-BDS-mixture when sufficiently mixed and afterwards easily separated in a simple decanter, protecting the enzyme from the harsh conditions in the stripper. In contrast to the enzyme beads an effective CA concentration of 0.2 wt.-% was well feasible with the BDS-solvent-mixture. The results from investigations at technical scale at TUDO and a direct comparison with the dissolved enzymes-solvent system are presented in Figure 19. Especially for higher liquid loads the BDS system reaches a comparable absorption performance as the dissolved enzyme system. It is envisioned that the BDS based system could be implemented together with conventional absorber-desorber configurations with minimal retrofitting and allowing continued use of thermal regeneration without damaging the enzyme-based biocatalyst, which could accelerate commercial deployment. Thus, future research should focus on this way of enzyme application for CO₂ capture processes.

Modelling of absorption with enzyme accelerated solvents

The most attractive strategy for enzyme application was to be evaluated based on the economic and environmental investigations in WP6&7. In order to allow for process design and evaluation, detailed rate-based models of the absorption and desorption columns have been developed on the basis of the experimental results at lab-scale and technical scale. Specifically for the desorption column dedicated experiments in a closed cycle plant at the Australian partner CSIRO were performed and evaluated. Finally, two alternative modelling approaches were developed by DTU and TUDO. While a simplified rate-based model was developed and implemented in the simulation environment Aspen Plus[®] by TUDO, which allowed a direct application into the process design workflow in WP6, a more detailed kinetic model incorporating enzyme inhibition by bicarbonate formation was established by DTU, allowing for validation of the results obtained by the simplified model. Both models were validated and showed sufficient accuracy, which is exemplarily depicted for the DTU model in a parity plot in Figure 20.

⁹ Bucholz, T. L.; Zaks, A.; Powell, D.; Weber, L.; Hulvey, M.; Reardon, J.; Rambo, B. (2015): Carbonic anhydrase xerogel particles (US20150099289 A1).

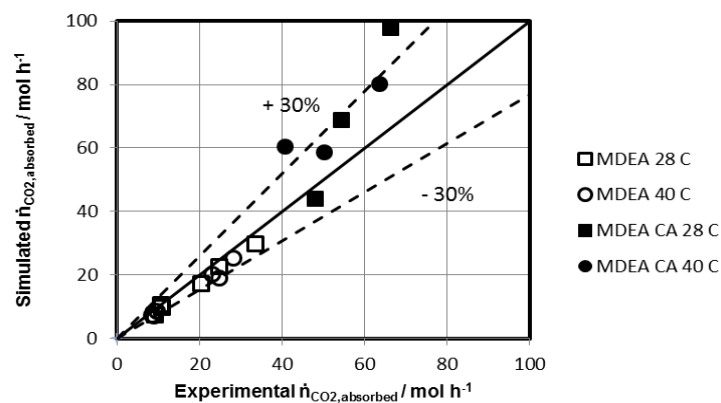


Figure 20: Parity plot between measured absorbed flux and simulation with DTUs CAPCO2 model with incorporated enzyme kinetics for pilot experiments performed by DTU.

Scale up of absorption with enzyme accelerated solvents

Considering industrial application of CO₂ absorption with enzyme accelerated solvents, scalability is a crucial issue. To address the question of scalability and the reliability of the data determined at technical scale additional scale-up studies were successfully conducted from technical scale (diameter 110 mm) to demonstration scale (diameter 422 mm) resulting in equivalent results, experienced at comparable experimental process conditions. The results are exemplarily illustrated in Figure 21, whereas due to the differing dimensions of the used absorbers the measured absorbed mole flow of CO₂ was normalized to the packing volume. Only for the lower F-Factor and low liquid loads a significant difference between the results obtained at the different scales was observed, such that scale up of applying enzyme accelerated solvents for CO₂ capture based on the technical scale experiments and the developed models is justified. The validation of the transferability of the performance results between technical and demonstration scale confirms that smaller scale testing in the university technical scale environment can be reliably used to predict larger demonstration scale performance, allowing optimizations at technical scale to be considered immediately relevant for larger demonstration scale tests, giving significant advantage in reducing time and resources for developing demonstration scale applications.

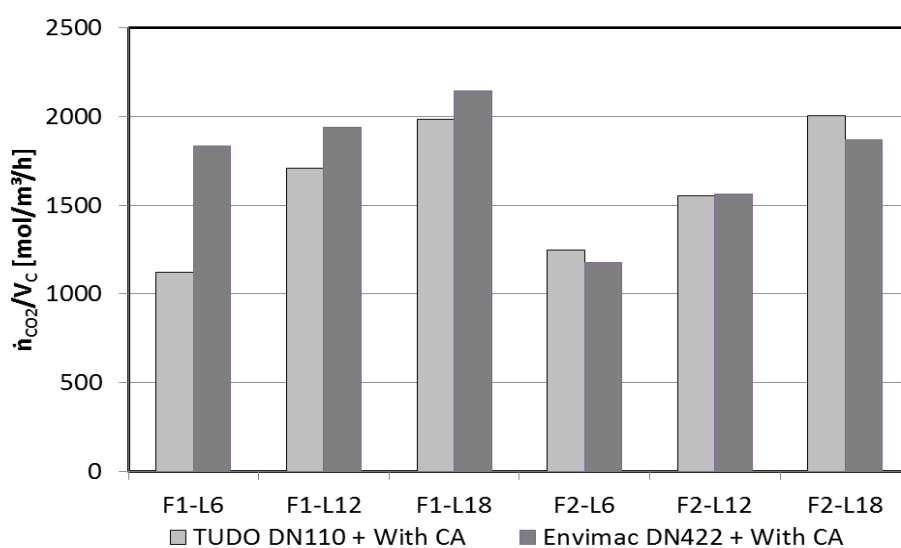


Figure 21: Comparison of absorbed mole flow of CO₂ between technical and demonstration scale.

WP5: Absorption in membrane contactors

In WP5 both newly developed PIL materials and enzyme-solvent systems were integrated into membrane contactors as innovative gas-liquid contacting equipment. The major benefits of the membrane contactor over columns is the provision of a well-defined and large (interfacial) surface area per volume in combination with a dispersion-free contact of the two phases (flue gas and absorption solution). The separation of the two phases by means of a porous membrane reduces solvent losses and allows for an additional flexibility concerning the operating pressure, flow rate and temperature of both, the incoming flue gas and the solvent solution. Of course there are also additional challenges that need to be resolved when applying membrane contactors, as material stability and surface properties need to be carefully selected and operating conditions need to be restricted in order to avoid breakthrough of one of the involved phases into the other.

Material systems selected and investigated

To maximize the merits of the membrane contactor, a proper selection of the combination of membrane material and liquid phase was made with regard to stability (resistance to both flue gas components and to solvent), mass transfer resistance, commercial availability, cost and environmental issues. The temperature stability limit of the enzyme of $\sim 60^{\circ}\text{C}$, defined the upper temperature limit and allowed for the use of a variety of membrane materials. Hydrophobic membranes were selected to ensure a suitable gas-liquid contact interface at the permeate side of the membrane and the chemical resistance to the solvent systems determined in WP2 was a further selection criteria. Based on these criteria a variety of membranes was screened and experiments were subsequently performed with commercially available hollow fibre polypropylene membrane modules and flat sheet composite fluoro-polymer membranes on polypropylene backing, providing higher chemical stability, which is known to be an issue for plain polypropylene membranes in long-term applications. Initial experiments at NOVOZYMES proved the polypropylene hollow fibre membranes to be compatible with the enzyme. Besides the most promising enzyme enhanced MDEA solvent system, the MDEA solution was also investigated as a reference case.

Furthermore, the coating of a selective PIL layer was investigated for the flat sheet membranes in order to provide a proof-of-principle demonstration of a hybrid membrane contactor, the principle of which is depicted in Figure 22. The most promising blend of PILs for this application is PolyDDATFSI/PYR14TFSI/Zn(II)TFSI.

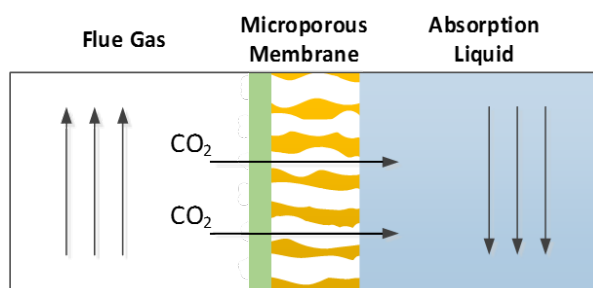


Figure 22: Hybrid membrane contactor system with added PIL selective layer (green) on the porous membrane (yellow) combined with enzyme activated absorption solvent.

Benchmarking of membrane contactor equipment

In order to compare the performance of flat sheet and hollow fibre membrane modules two membrane contactor rigs were designed, constructed and conditioned at TUDO and SINTEF as

shown in Figure 23. Benchmarking of the membrane contactor equipment was performed at 25–35°C using 30 wt% MEA solution without enzymes, applying hollow fibre membrane modules with active area of 1.045 m² and flat sheet membranes of 12.6 cm².

Standardized experimental procedures were established for the investigation of the membranes through critical pressure measurement of several candidate membranes. Due to the different nature of the membrane modules, the applied flow rates and pressure difference were determined specifically for each set-up. As expected, the more dense structure of the flat sheet composite fluoro-polymer membranes resulted in a lower area-specific molar flow of absorbed CO₂ (0.35 to 0.88 mol·hr⁻¹·m⁻²) as compared to that of the more open porous hollow fiber polypropylene membranes (11.0 to 22.9 mol·hr⁻¹·m⁻²). However, the fluoro-polymer membrane provides greater long term durability to the amine based solvents and is less prone to biofouling by the enzyme. No comparable membrane was commercially available in the case of hollow fibers. The benchmarking test results were therefore mainly applied as baseline experiments for the further investigations on the individual test rigs.

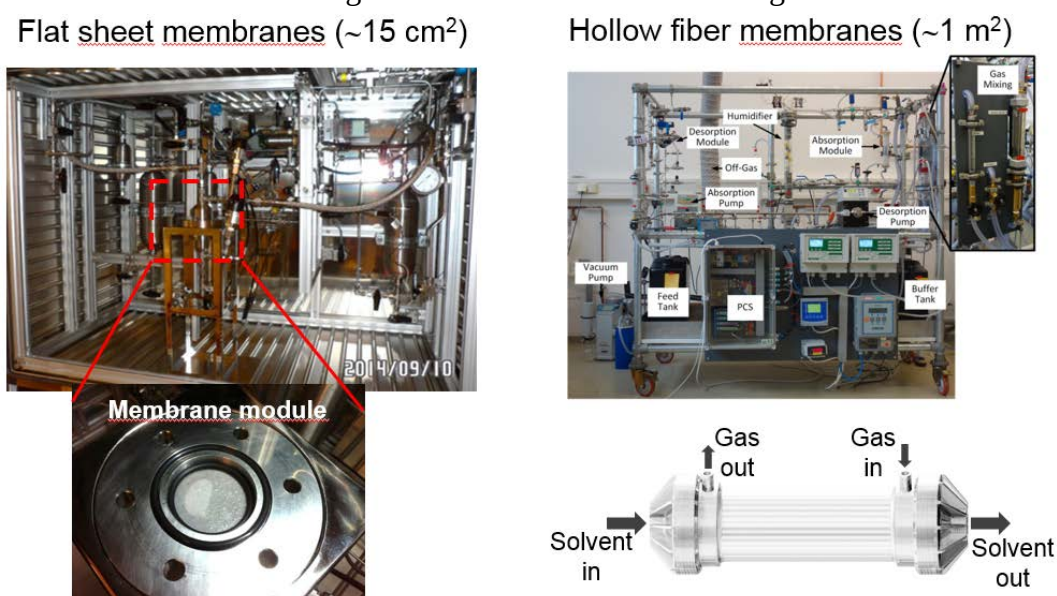


Figure 23 Membrane contactor test rigs for flat sheet and hollow fibre membrane modules

Enzyme activated CO₂ absorption with membrane contactors

Similar to the absorption in columns mass transfer was determined with and without the addition of the enzyme in MDEA solvent systems. However, the results indicated in Table 3 for both flat sheet membranes at 35°C and hollow fiber membrane modules at 40°C illustrate that the catalytic effect due to the addition of enzymes, while being comparable for both membrane configurations is significantly lower than experienced in columns. It seems reasonable that the hollow fiber membranes allow for higher flux of CO₂ due to a more open pore structure (larger pore size) than the investigated more dense flat sheet membranes. The obtained absorption rates were comparable to several reports from literature, e.g. from Hoff et al.¹⁰ (0.24 mol CO₂/m²/hour @ 40°C using PTFE membranes and 30%MDEA + 5%Piperazine) and Wang et al.¹¹ (0.36 mol/m²/h @ 25°C using hollow fiber membrane contactor and 30% MDEA), being in the same range as the applied flat sheet membranes while the results for the hollow fiber membranes are an order of magnitude higher. It is assumed that the lower

¹⁰ Karl Anders Hoff, et al., Chemical Engineering Science **116** (2014) 331–341

¹¹ Z. Wang et al., Chemical Engineering Science **93** (2013) 238–249

catalytic effect can be attributed to a steric hindrance limiting the enzymes approach to the gas-liquid interphase located in the pores of the membrane. The current results are further backed up by similar enhancements from introduction of enzymes in the solvent for absorption in membrane contactor reported by Cowan et al.¹². A closer fundamental study of enzyme-membrane interface behavior could lead to developments that improve the catalytic effect of CA in membrane-based systems.

Table 3: Absorption rates (= CO₂ flux) for flat sheet and hollow fiber membrane modules from comparable experiments using 30 wt.% MDEA solution and feed gas of 15% CO₂ in N₂.

Membranes	Solvent system	Temperature	CO ₂ flux (mol/m ² /h)	Catalytic effect
Flat sheet	30% MDEA	35°C	0,11	1
Flat sheet	30% MDEA w/CA	35°C	0,19	1.67
Hollow fiber	30% MDEA	40°C	2,33	1
Hollow fiber	30% MDEA w/CA	40°C	4,05	1,74

Proof-of-concept of CO₂ absorption with hybrid membrane contactor

While the addition of a dense PIL layer to the membrane contactor provides additional mass transport resistance the high selectivity of the PIL as sorbent may result in improved performance especially considering potential synergies with the enzyme enhanced solvent. The concept of such a hybrid membrane contactor (cf. Figure 22) was therefore investigated for the optimal PILs developed in WP1 and investigated for gas membranes in WP3. After evaluating various configurations of the membrane contactor with the additional PIL layer a proof-of-principle for enhanced absorption rate in a hybrid membrane contactor was demonstrated using PIL material F9:1.

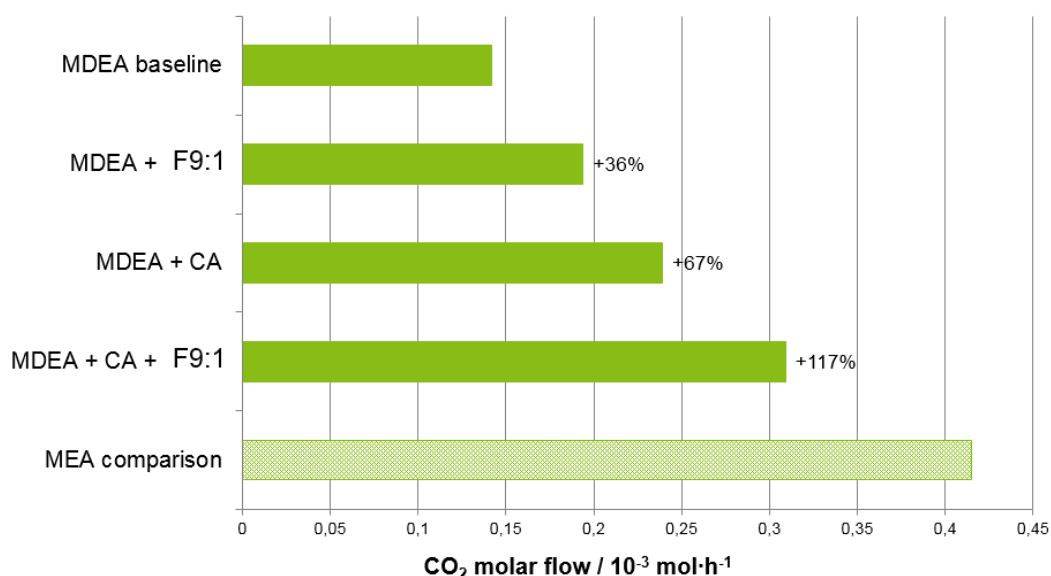


Figure 24: CO₂ molar flows from absorption in membrane contactor using flat sheet membrane with and without selective PILs layer and 30% MDEA with and without enzyme. MEA reference added for comparison.

¹² R. M. Cowan et al., <https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/43084-CCS-Conference-May-2009.pdf>

As shown in Figure 24, an enhancement of the absorption rate of 36% was found when adding the selective PIL layer and using 30% MDEA solution as solvent, while the combination of enzyme activated MDEA solution and a PIL layer resulted in more than twice the CO₂ absorption compared to the MDEA baseline.

CO₂ desorption with membrane contactor

Membrane contactor allows for two modes of operation for stripping, one is the application of sweep gas (N₂ or air), the other is the application of slight vacuum on the permeate side. Desorption with sweep gas was performed for both flat sheet and hollow fiber membranes. Despite some differences in the operation conditions concerning mainly the pressure difference the measurement with CO₂ loaded 30% MDEA solvent at 60°C gave comparable results. Application of a slight vacuum (0.80-0.98 bara) was tested in the case of flat sheet membranes which resulted in considerably higher desorption rates. Key figures of the performed experiments are presented in Table 4. While experimentally more challenging, the work with a slight permeate vacuum demonstrates the potential for applying the membrane contactor technology also for CO₂ desorption, however this may not be realistic with the large volumes of flue gas to be processed at a typical coal fired power plant. It may be more realistic to consider the use of the membrane contactor for absorption and carry out desorption using alternative methods.

Table 4: Desorption rates obtained with membrane contactor from CO₂ loaded 30% MDEA solvent at 60°C.

Membranes	Solvent system	Desorption mode	CO ₂ flux (mol/m ² /h)	Catalytic effect
Flat sheet	30% MDEA	Sweep, $P_{\text{gas}} - P_{\text{liq}} \approx 0.15$ bar	0,08 – 0,14	-
Hollow fiber	30% MDEA	Sweep, $P_{\text{liq}} - P_{\text{gas}} \approx 0.15-0.40$ bar	0,15 – 0,19	-
Hollow fiber	30% MDEA w/CA	Sweep, $P_{\text{liq}} - P_{\text{gas}} \approx 0.15-0.40$ bar	0,33 – 0,40	2,13
Flat sheet	30% MDEA	Vacuum, $P_{\text{liq}} - P_{\text{gas}} \approx 0.40-0.60$ bar	1,4 – 5,4	-

Modelling and simulation of transport phenomena and mechanisms

In order to allow for process design and evaluation also a model of the membrane contactor for CO₂ absorption was developed. The model, which is structured in three hierarchical levels as shown in Figure 25 (left), was developed using Aspen Custom Modeler (ACM) in order to describe mass transfer of CO₂ absorption/desorption in membrane contactors and allow for easy integration within the process design approach undertaken in WP6. The model considers an adjusted gas-liquid equilibrium model that accounts for the effect of liquid loading, as well as energy balances in order to give a more accurate prediction of the absorption rates and temperature profiles over the contactor length. An experimental validation of the model was performed for the ternary system MEA-H₂O-CO₂, where the accuracy of the model is indicated by the parity plot illustrated in Figure 25 (right), in which experimental results are compared with the predictions from the model. The model is capable of accurately predicting the absorbed molar flow of CO₂.

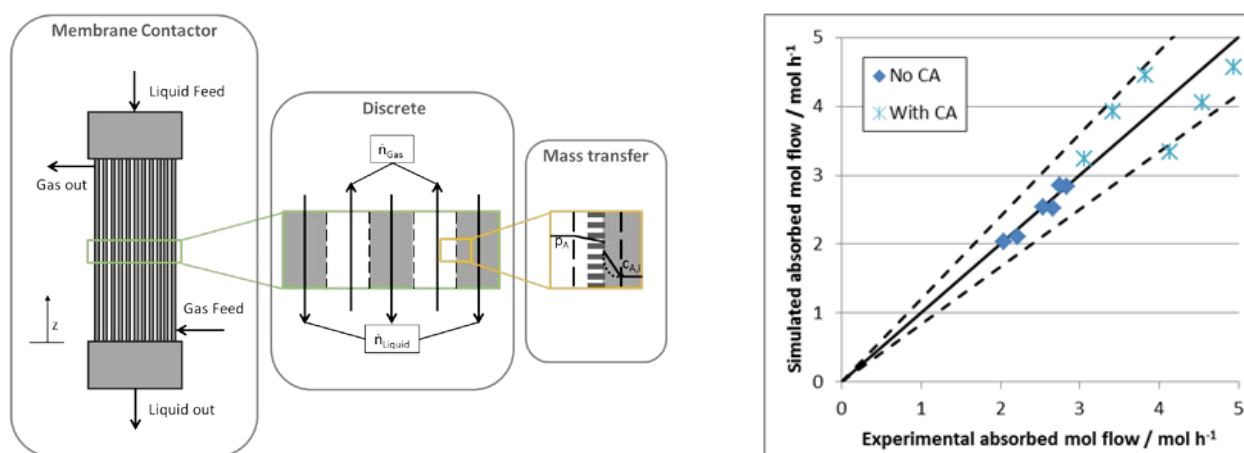


Figure 25: Structure of the membrane contactor model with the different hierarchical levels (left) and parity plot of the absorbed mol flow of CO₂ in membrane contactor (right)

Effect of real flue gas contaminants

In order to evaluate the applicability of the developed membrane contactor under realistic conditions, including the use of flue gas components like SO₂ and NO_x, the tolerance of the individual components i.e. membrane materials and enzyme-solvent systems towards such components were tested. The flat sheet membranes applied for absorption/desorption and the hybrid membrane contactor materials have been tested as a regular gas separation membrane using more realistic conditions of 15% CO₂ concentrations, 5% O₂, 100% relative humidity and eventually 300 ppm of SO₂. The performance of the hybrid membrane contactor material was stable over a time frame of >1500 hours. In addition the activity of the enzyme in the solvent system upon exposure to SO₂ and NO_x was tested. Judging from esterase and CO₂ assays the enzyme carbonic anhydrase showed no degradation of activity for hydration of CO₂ or hydrolysis of p-nitrophenyl acetate (pnp) during short term exposure of up to 4 hours to SO₂ (20-100 ppm) and NO_x (180-360 ppm). The enzyme remains active also after extended exposure tests up to 45 hours with 100 ppm SO₂, although a significant drop of activity towards hydration of CO₂ was observed.

WP6: Process development

The activities of process development aimed at the design of novel and competitive process concepts for post-combustion carbon capture based on the highly innovative technologies and materials developed in the INTERACT project. In the course of those activities an integrated approach building on the experimental results obtained in WP3-5 and simulation-based process analysis (WP6) was applied to generate a fundamental understanding of the technologies considered.

Exploiting these deep insights promising process concepts on INTERACT post combustion technologies were identified. To tap their full potentials process simulation was conducted facilitating analysis, debottlenecking and optimization of these concepts from an energy and/or economic perspective. Mathematical models developed for each individual INTERACT technology were applied. The most promising process concepts, which were evaluated as such in WP7 under industrial conditions, are further presented in some detail.

Absorption/desorption using enzyme activated MDEA-solvents

As a result of work of WP 2 and 4 it became obvious that the chemical absorption of carbon dioxide using solvent mixtures that store CO₂ in form of bicarbonates prospers from the addition of a catalytically active enzyme. The presence of the enzyme accelerates the formation and decomposition of bicarbonates; even at reduced temperatures equilibrium loading conditions are virtually obtained during absorption and regeneration which allows for larger cyclic loadings and thereby for an economically attractive reduction of the amount of the solvent utilized.

While the presence of the enzyme facilitates the operation at more favorable, hence lower, absorption temperatures it adds new constraints to the process. Among others, the most essential constraints to be addressed by process development are related to the temperature-sensitivity of the enzyme as well as to the ability to cool down gas and liquid feeds of the absorber at industrial conditions to temperatures that cannot be reached using cooling water in conventional set-ups.

In a structured manner various process concepts were developed to tackle the aforementioned constraints while exploiting the benefits of the innovative technology. Figure 26 provides an overview on these process concepts.

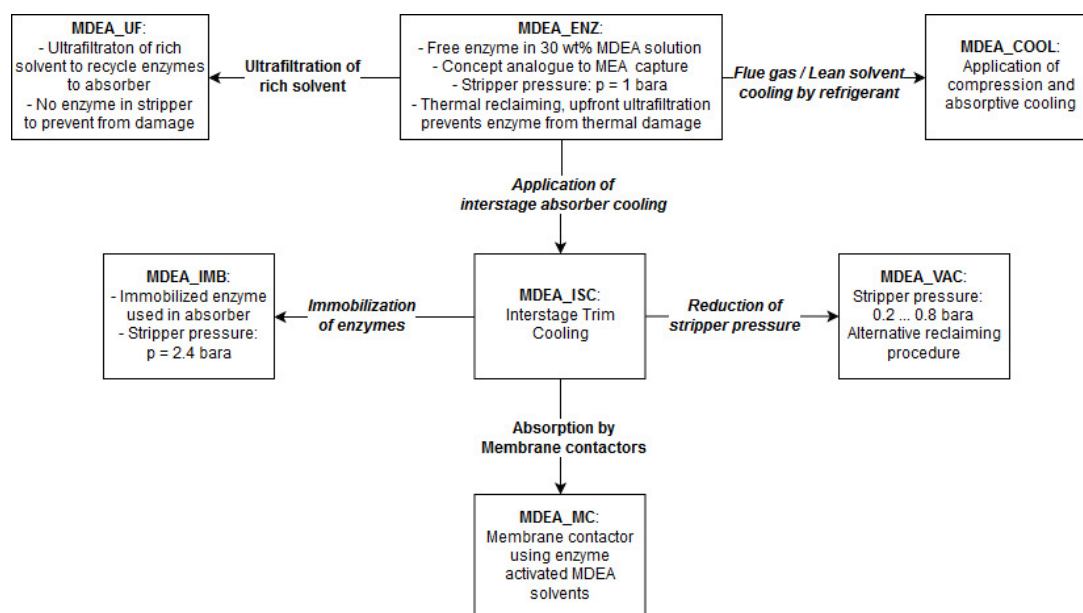


Figure 26: Overview on types of enzyme activated process concepts investigated.

Initially starting from the application of the conventional process concept known from MEA-based carbon capture (MDEA_ENZ), modifications were performed to boost the performance of the capture process: The process alternative MDEA_COOL makes use of a chilled utility, generated from absorption or compression cooling, to reduce the temperature of the absorber feed streams. The potential benefits of this set-up are found from the trade-off between energy savings due to exploitation of larger cyclic CO₂-solvent loads and the energy demand of refrigerant generation.

In contrast, the process MDEA_ISC prevents from the use of chilled utilities. Efficient cooling is conducted by application an external inter-stage cooler attached to the absorber. By this non-conventional arrangement heat rejection is intensified as thermal energy originating from absorption in the upper section of the column becomes removable by cooling water. Both concepts are illustrated in Figure 27.

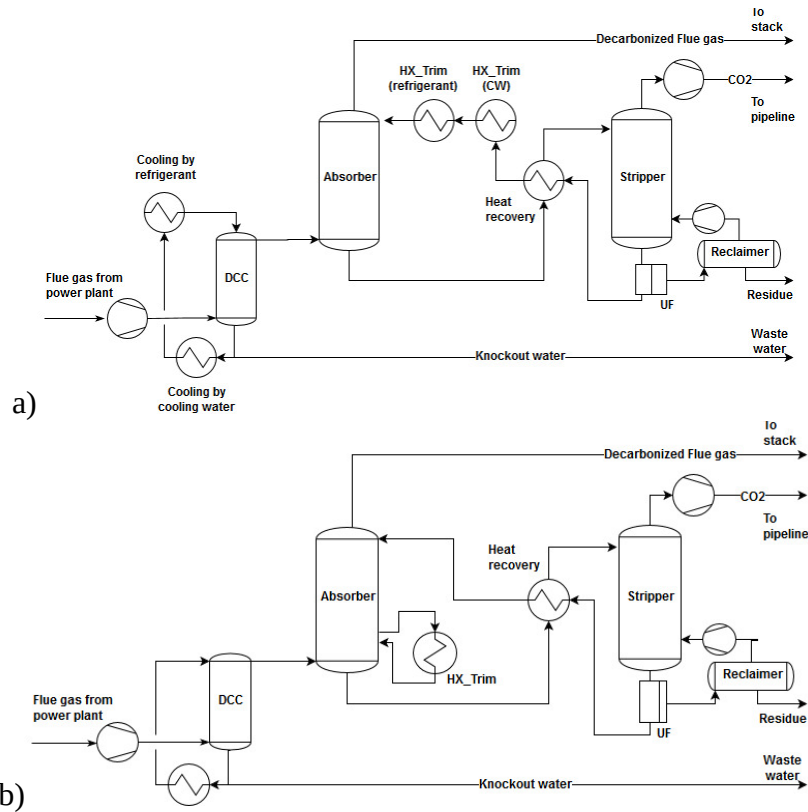


Figure 27: Process concept of the process MDEA_COOL (a) and MDEA_ISC (b).

To protect the sensitive catalyst from thermal damage in the hot section of the process, hence inside the stripper, the immobilization or reclamation of the enzyme inside the low temperature process section was investigated. Figure 28 illustrates the process configuration MDEA_IMB which uses immobilized enzymes as catalyst in the absorber. Moreover, the configuration MDEA_UF applies ultrafiltration to restrain the free enzymes in the "cold" section of the process.

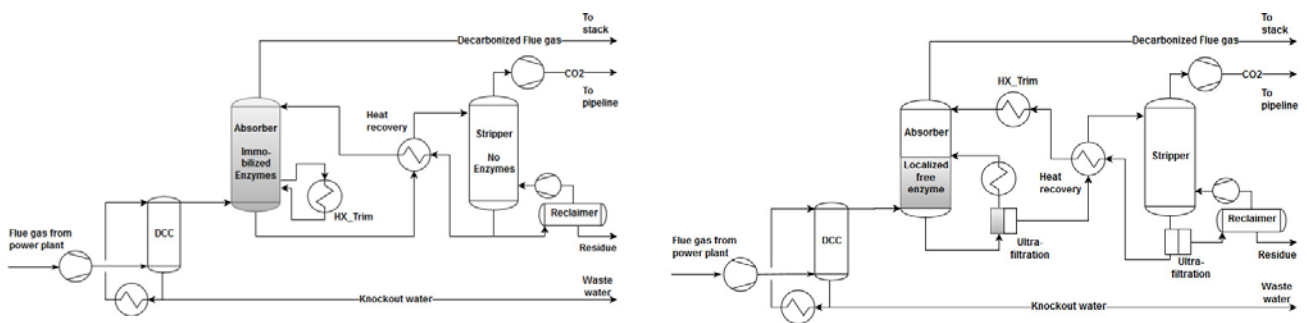


Figure 28: Process concept of the process MDEA_IMB (left) and MDEA_UF (right).

In addition to the exploitation of conventional columns for decarbonization and solvent regeneration, the usage of more sophisticated technologies such as membrane contactors were investigated. The membrane contactor was applied to replace the conventional absorber, the desorber or both of them, respectively.

Gas separation membrane processes

The application of INTERACT-gas separation membrane technology allows for the selective removal of a target component, CO₂, from a feed stream. Three alternative process concepts were developed distinguishing between processes with and without sweep gas use: A single stage-membrane process were designed, whereas driving forces for transmembrane separation are created by feed gas pressurization and vacuum conditions on the permeate side. No sweep gas was used. Since the simultaneous realization of numerous targets such as high CO₂ capture rates and stringent purities of the product streams is challenging using a single stage process only, a 2-stage membrane process was considered as well. The subsequent membrane operations supplement each other, whereat the upstream membrane focuses on the decarbonization of the flue gas to a sufficient extend, while the second membrane stage purifies the pre-concentrated CO₂ rich permeate stream from the first stage to a composition that allows long-term CO₂-storage. The concepts are illustrated by Figure 29 (a) and (b).

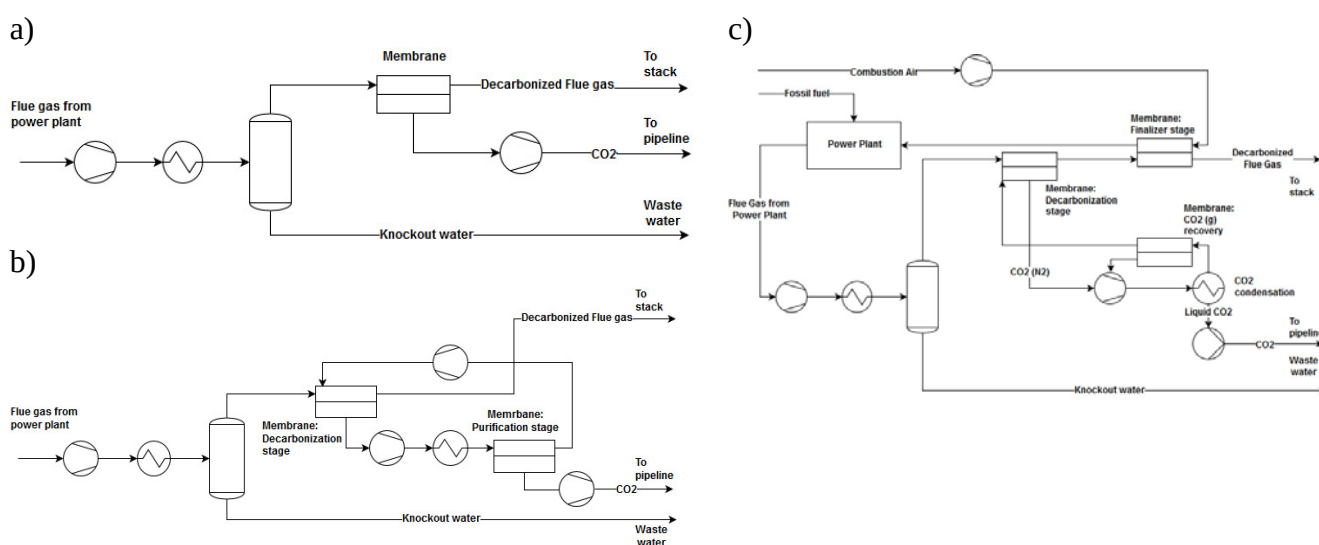


Figure 29: Process concept of the process single stage membrane process (a) the 2-stage membrane process (b) and the MTR-membrane concept.

Different from the two aforementioned membrane process alternatives, the MTR-membrane process concept applies exhaust gas recirculation. The process, using a sweep gas to support the off gas decarbonization, is illustrated by Figure 29 (c). The process utilizes an assembly of three membrane operations to generate a CO₂ rich stream at CCS conditions and is applicable for the decarbonization of power plants. Its concept is rather simple: the flue gas of the power plant is compressed and conditioned. By an upstream membrane separation carbon dioxide is recovered from the flue gas along with other components, mainly nitrogen. The resulting permeate stream is fed to a CO₂-compression train; at high pressure carbon dioxide is condensed, separated from the gas stream and prepared for pipeline transport.

Naturally, the removal of CO₂ by condensation from the compressed gas stream is incomplete. Thus, for efficiency reasons, the remaining gas fraction is processed by a second membrane operation that aims at the recovery of compressed CO₂. While the permeating gases are recycled into the compression train, the retentate stream is mixed into the upstream flue gas stream.

In contrast to the other membrane processes reported, no deep flue gas decarbonization is targeted by the operation of the upstream membrane ("Decarbonization membrane"). Accordingly, a significant amount of CO₂ is found in its retentate stream. To comply with the envisioned capture rate this product stream is directed to a successive membrane unit. Here, the remainder of CO₂ is majorly

removed from the flue gas; carbon capture at an aimed rate is realized. The operation is supported by the presence of a sweep gas. Using the combustion air of the boiler as diluting agent provides numerous benefits since neither extra sweep gas generation nor downstream separation of the CO₂ from the diluting gas stream is required. Via the off gas of the boiler the collected carbon dioxide is recycled to the capture facility and becomes available for removal.

Adsorption using the solid, PIL-coated beads

In addition to the absorption/desorption- and gas separation membrane processes a further process concept based on adsorption was developed. This process exploits the PIL-based sorbents as solid inventory that were developed in WP1. The new material exhibits a reasonable adsorption capacity of carbon dioxide and shows a good CO₂/N₂-selectivity. To exploit this technology for post combustion carbon capture a promising pressure swing adsorption (PSA) process was designed. The process concept that is illustrated by Figure 30 comprises of two adsorption stages. The first stage decarbonizes the flue gas. The decarbonized gas is directed to the stack for release. By pressure reduction a pre-concentrated stream of CO₂ is generated. After the pressurization of this stream, gas treatment is conducted by a second PSA stage, where CO₂ is selectively adsorbed. Since the removal of carbon dioxide is incomplete the breakthrough gases are recycled upstream. By the regeneration of the loaded sorbent of the second stage a CO₂ rich stream at desired concentration is produced by pressure reduction. This stream is compressed to pipeline pressure.

To facilitate a continuous operation and to improve the energy efficiency of the process each PSA stage operates multiple columns in parallel. Benefiting from a sophisticated schedule of pressurizing and depressurizing operations the dynamic behavior is smoothed out and the process operates close to steady-state conditions.

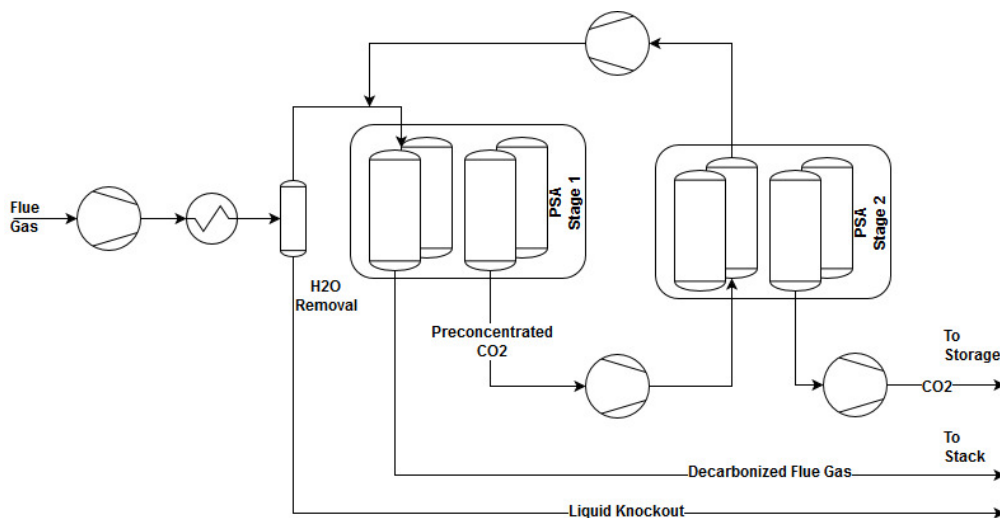


Figure 30: Process concept of the PSA capture process.

WP7: Assessment of new technologies in industrial application scenarios

To allow for a significant quantification of the performances of the novel post combustion carbon capture technologies developed under the umbrella of the INTERACT project a system-integration into an industrially relevant CO₂ emission scenario was performed. Mass and energy balancing were carried out and the each integrated process concept was optimized. The framework of the investigation has been derived from the guidelines of the European Benchmark Task Force (EBTF) and was applied likewise to all process alternatives under consideration.

The resulting energy and mass balances formed the bases of the techno-economic as well as environmental analysis of the process performances. For a fair comparison, the outcome is benchmarked against the Base Case, which is a capture process that uses state-of-the-art technology. Following the recommendations of the EBTF core document “European best practice guidelines for assessment of CO₂ capture technologies” an Advanced Supercritical Pulverized Coal-fired power plant acted as such emission scenario. The MEA-based absorption/desorption process served as the Base Case to benchmark the performances of the innovative technologies.

Whole process simulation

Under the umbrella of the aforementioned techno-economic framework all innovative as well as standard post combustion capture technologies were simulated using the commercially available simulation environment Aspen One V8.8. For each technology system-integration into the power plant scenario took place; mass and energy integration was performed. All process alternatives were investigated at a similar level of detail and were optimized with respect to technical feasibility, robustness, energy efficiency and costs.

Techno-economical assessment

Based on the energy and mass balances obtained from the simulation activities the techno-economic performances of the various technologies were quantitatively assessed. Table 5 summarizes the outcome of this assessment with regard to the most promising representatives of each INTERACT technology under investigation. Along with that the corresponding calculation results of the Base Case capture process are presented.

Most encouraging results are found: for each INTERACT technology option at least a single process concept was identified that outperforms today’s standard technology (Base Case) from an efficiency perspective. But even more so, taking into account the possible reduction of the energy penalty by ~3.5% points and the reduction of CO₂ avoidance cost by ~15% the INTERACT technologies present a breakthrough in post combustion carbon capture in terms of net power output, energy penalty and costs of electricity production.

Table 5: Overview on the techno-economic results obtained on the best performing representatives of innovative INTERACT CO₂ capture techniques. In addition information on the standard technology (Base Case) is provided.

		Base Case	Enzyme-activated MDEA-solution	Gas separation membrane	Membrane Contactor (using enzyme-activ. MDEA-solution)	PIL-based PSA
Total Plant Costs	[Mio€]	1484	1568	1763	2397	2083
Gross Power Output	[MW _e]	685,17	756,40	819,42	756,22	819,42
Net Power Output	[MW _e]	551,54	609,77	576,76	601,17	583,13
Net Elec. Efficiency	[%]	32,90%	36,37%	34,50%	35,86%	34,78%
Energy penalty	[%-points]	12,17%	8,69%	10,56%	9,20%	10,28%
SPECCA	[MJ _{LHV} /kg _{CO2}]	4,40	2,80	3,65	3,01	3,49
Costs of Electricity	[€/MWh _e]	85,19	81,37	90,95	122,10	105,43
Costs of CO ₂ avoided	[€/ton CO ₂]	46,95	40,63	55,66	100,48	76,52

While the results of the technical evaluation are apparent and easy to interpret, the findings obtained by the economic assessment require a more detailed breakdown due to its diversity; in particular with regard to the capital investment, the costs of electricity production and CO₂ avoidance costs. The solvent based processes exploiting conventional columns to conduct CO₂ capture and recovery require capital investments in the range of the Base Case. Significant reductions in electricity

generation costs and CO₂ avoidance costs are estimated. Savings up to 4 €/MWh_e (costs of electricity production) or 6 €/ton_{CO2} (avoidance costs) seem realistic. In contrast to the solvent based processes, the assessments of the membrane-based and adsorption-based processes indicate elevated investment costs. This increase is inflicted by the predicted size of membrane area and the estimated amount of solid inventory as both are consumed in large quantities and acquired at comparably high specific purchase prices. In addition, concerning these technologies, periodically follow-up investments are required due to the limited lifetime of the core materials. As a consequence, the costs of electricity generation and CO₂ avoidance are found in the range of the Base Case.

Among all technologies investigated, membrane contactors in combination with enzyme-activated MDEA-solvents stand out since electricity is generated at a significantly higher price. In this case CO₂ avoidance is more costly than in MEA-based technology. This difference results from the large share of investment costs allocated to purchase tremendous amounts of the required membrane area. For the time being it is theorized that the astonishingly high demand on membrane area is attributed to an adverse interaction between the enzyme that intensifies the absorption of CO₂ and the selected membrane material. In that sense it needs to be understood that the findings represent the performance of a unique combination of materials and technologies and therefore do not allow drawing general conclusions on the performances of membrane contactors in the field of carbon capture.

Life cycle assessment

Based on the characterization of the benchmark process and the techno-economic optimization of the different process concepts a life cycle assessment (LCA) was performed to evaluate the environmental impact of the different processes. A summary of main steps of the LCA application to INTERACT CO₂ capture alternative processes is given in Table 6.

Table 6: Summary of main steps, selections and assumptions for LCA application to INTERACT CO₂ capture alternative processes

LCA step	Description
Full scenario definition and description	A reference case was selected and characterized, an Advanced Super Critical (ASC) pulverized fuel bituminous power with a generation capacity of 819,8 MW _e (gross), a net output of 757,1MW _e and a net cycle efficiency of 45,2%.
Functional unit definition	Definition of the functional unit as 1 MWh _e of electricity delivered by the plant to the grid.
Scope definition	The LCA is performed following a Cradle-to-Gate approach; the system boundaries of the LCA include the extraction and processing of the coal and other raw materials, the production of electricity, the capture of carbon dioxide and the treatment of the present wastes.
Data sources definition	The data used to perform the LCA analysis has been taken from the documentation regarding the Common Framework delivered by EBTF and the simulation reports of the different process delivered by SUPREN under the scope of the INTERACT project.
Key assumptions	All the assumptions regarding the consideration of workforce, capital equipment, relevant flows, storage or use for captured CO ₂ etc., are primary based on the recommendations given by the EBTF in the Common Framework Definition Document
LCA software	The calculation regarding the LCA tasks within the INTERACT

selection	project were conducted using the software SimaPro developed by Pré Consultants, the leading LCA software chosen by industry, research institutes, and consultants world-wide
Lifecycle inventory	In the course of data collection the database Ecoinvent 3.2 was extensively used for characterizing impacts and footprints of substances present in inlet and outlet streams of the processes.
Lifecycle impact assessment	Midpoint and endpoint impact categories were selected for impact assessment, allowing the interpretation of the final results of the selected alternatives.

The results of the LCA were evaluated based on the calculated midpoint and endpoint indicators, which are illustrated for the Base Case and the most promising process concepts in Table 7 and 8. From the interpretation of the estimated midpoint indicators it becomes clear that carbon capture prospers from the application of the novel INTERACT process technologies; in particular with respect to environmental impact categories such as “climate change”, “freshwater eutrophication”, “human toxicity”, “photochem. oxidant formation” (with the exception of PSA + PIL process) and “fossil depletion”.

Table 7: Midpoint categories results for environmentally best performing INTERACT CO₂ capture process alternatives (90% CO₂ capture rate)

Impact category	Unit	BC MEA	MDEA + free enzymes	MDEA + immobilized enzymes	1000 GPU PIL Membrane	MDEA + Membrane Contactor	PSA + PIL
Climate change	kg CO ₂ eq	241,47	220,78 -8,57%	231,88 -3,97%	226,27 -6,29%	224,09 -7,20%	241,24 -0,10%
Terrestrial acidification	g SO ₂ eq	1.759,39	2.436,30 38,47%	2.496,39 41,89%	1.951,29 10,91%	2.461,68 39,92%	2.133,63 21,27%
Freshwater eutrophication	g P eq	556,3	507,55 -8,76%	519,35 -6,64%	527,99 -5,09%	511,55 -8,04%	539,02 -3,11%
Marine eutrophication	g N eq	265,12	276,29 4,21%	283,45 6,91%	700,22 164,11 %	280,12 5,66%	556,47 109,89 %
Human toxicity	kg 1,4-DB eq	400,79	365,78 -8,74%	380,56 -5,05%	380,28 -5,12%	368,95 -7,94%	392,77 -2,00%
Photochem.oxidant formation	g NMVOC	1.900,48	1.735,29 -8,69%	1.786,41 -6,00%	1.820,01 -4,23%	1.752,08 -7,81%	1.939,36 2,05%
Particulate matter formation	g PM ₁₀ eq	628	682,29 8,64%	717,11 14,19%	651,18 3,69%	689,85 9,85%	708,94 12,89%
Water depletion	l	2.036,23	2.698,16 32,51%	2.814,82 38,24%	2.864,86 40,69%	2.785,21 36,78%	3.162,77 55,32%
Fossil depletion	kg oil eq	264,73	241,39 -8,82%	245,83 -7,14%	249,51 -5,75%	243,59 -7,99%	259,07 -2,14%

To ease the understanding of the outcome of the LCA endpoint indicators are used which are simpler to interpret. These endpoint indicators represent a sum of the mid-point categories weighted according to their significance. The resulting end-point indicators imply that for each INTERACT CO₂ capture technology essential improvements regarding the environmental impact are identified, outperforming the benchmark process. The main midpoint contributors to the endpoints are fossil depletion, climate change, human toxicity and particle matter formation. To provide a distinct quantitative example, for the process concept MDEA + free enzymes more than 98 % of the total end-points can be attributed to the mid-point categories fossil depletion (≈57%), climate change (≈22%), human toxicity (≈11%) and particle matter formation (≈8%). This leaves a remaining 2% contribution for the rest of the mid-point categories. Therefore, the large relative increases in marine eutrophication and water depletion, which is listed for some of the process concepts in Table 7, has only modest influence on the environmental impact characterized by the endpoint categories.

Table 8: Endpoint categories results for environmentally best performing INTERACT CO₂ capture process alternatives (90% CO₂ capture rate)

	BC MEA	MDEA + free enzymes		MDEA + immobilized enzymes		1000 GPU PIL Membrane		MDEA + Membrane Contactor		PSA + PIL	
Human Health	15,21	14,45	-4,97%	15,13	-0,50%	14,63	-3,76%	14,62	-3,84%	15,51	2,00%
Eco-systems	4,93	4,53	-8,12%	4,75	-3,69%	4,63	-6,14%	4,60	-6,79%	4,94	0,13%
Resources	28,54	26,03	-8,80%	27,03	-5,29%	26,90	-5,75%	26,27	-7,95%	28,01	-1,86%
TOTAL	48,68	45,01	-7,53%	46,91	-3,63%	46,16	-5,17%	45,49	-6,55%	48,45	-0,46%

For a better visualization Figure 31 presents the relative environmental improvements compared to the Base Case. Obviously each of the process concepts presents an improvement concerning the environmental impact, whereas the estimated improvements are maximized for the enzyme activated reactive absorption processes with dissolved enzyme.

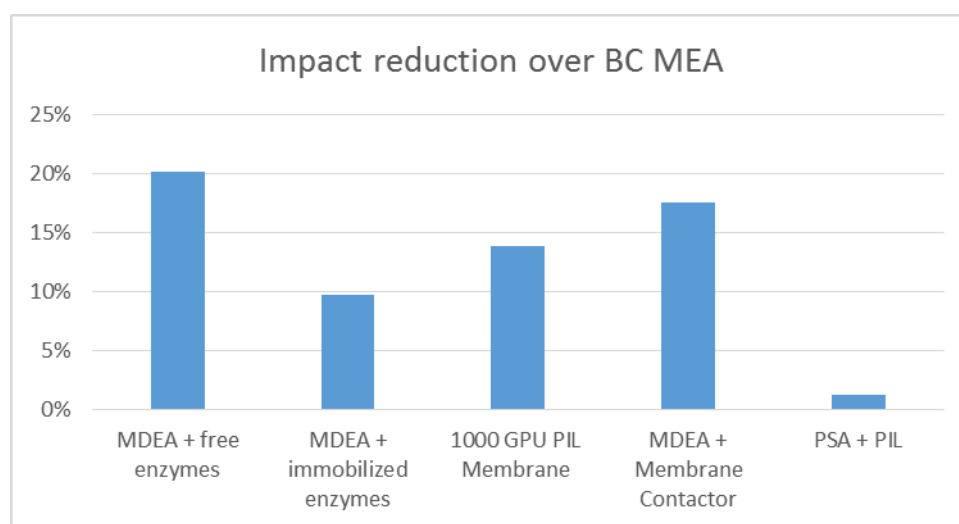


Figure 31: Impact reduction for environmentally best performing INTERACT CO₂ capture process alternatives over benchmark process

Conclusion: Concise assessment of the process concepts from techno-economic and environmental perspective

On the basis of the aforementioned findings, it can be concluded that among the investigated technologies the absorption/desorption process exploiting enzyme activated MDEA-solvents provide the biggest potential for competitive and environmental friendly carbon capture; overcoming the considered standard capture technology, i.e. MEA-based CO₂-absorption, by far. A significant reduction on the energy penalty of the CO₂ capture process ($\approx -3,5\%$) has been presented, associated with a decrease in the electricity production costs ($\approx -4,5\%$) as well as the costs of CO₂ avoidance ($\approx -13,5\%$) and a low environmental profile ($\approx -7,5\%$, endpoint indicators). Taking into account that the process concept can be implemented with established gas-liquid contacting equipment, for which successful scale-up studies were performed within WP4, provides further prospect towards successful implementation from a technical feasibility and robustness point of view.

Gas membrane separation, enhanced by a PIL coating, has been found to be less competitive in economic terms ($\approx +7\%$ electricity production costs, $\approx +18\%$ costs of CO₂ avoidance). However its

promising environmental impact (~-5%) and the opportunity for future improvement of this technology becoming more mature show a clear potential for a successful application. In particular, applications aiming at reduced CO₂ capture rates, as in such as CO₂/CH₄ for biogas upgrading or natural gas refinery, seem promising.

Despite the potential reduction of the energy penalty and potential improvements in terms of environmental potential, the developed pressure swing adsorption process based on PIL-impregnated beads, and the membrane contactor based enzyme-activated MDEA reactive absorption/desorption process require further development to compensate economic disadvantages when compared to the base case and commercially available alternative materials. Further development might however foster further exploitation of the potential and result in additional improvements, taking into account further optimized PILs and improvements in terms of the concept of hybrid membrane contactors, which was developed as a proof-of-concept in the scope of the INTERACT project and provides further potential for optimization.

The potential impact and the main dissemination activities and exploitation of results

Improved materials and production techniques for a targeted functionalization of tailored gas separation membranes

In the INTERACT project various synthetic strategies have been pursued for the development of a range of dense ILs to be used as active material in gas separation, membranes. The materials have been screened for CO₂/N₂(main flue gas components) separation, at lab scale but also for other aspects, such as the scalability and economic feasibility, that have major impact for the industrial production. Poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (polyDDATFSI), one specific PIL material, combined with ionic liquid and salt additive excelled in the preliminary tests at lab scale, where special attention was paid to the synthetic scalability, defect-free membrane formation capability, mixed gas selectivity ($\alpha_{\text{CO}_2/\text{N}_2} = 34$), and permeability of CO₂ (P=217-464 Barrer).

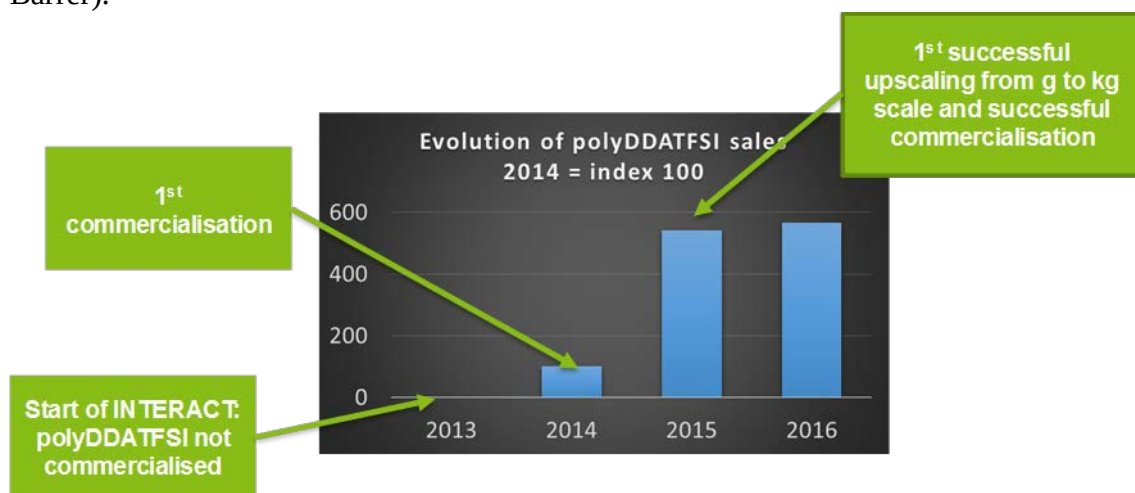


Figure 32: successful commercialisation of polyDDATFSI

It was observed that the gas separation properties of PIL-based membrane materials can be tuned by the incorporation of free ionic liquid and metal additives. Based on the positive results of the scale-up studies, **successful commercialization of this selected PIL, polyDDATFSI**, has started. The product is now in SOLVIONIC portfolio and is available up to the kg scale. As shown on Figure 32, the WP1 upscaling work was linked to the volume of sales of polyDDATFSI over the last few years.

Interestingly the developed PIL material has raised most **interest** so far **in the frame of electrochemical energy storage systems** (metal-ion battery applications, e.g. Li-ion batteries) as a component of gel/polymer based electrolytes rather than CO₂ capture processes, for which the material was initially developed in the project.

A range of this type of composition was marketed to the attention of the new generation of battery producers. Polymer electrolytes (PE) are membranes composed of a dissolution of salts in a polymer matrix with high molecular weight, whereas gel type electrolytes contain ionic liquid to enhance the ionic conductivity. Ionic liquids (ILs) and PILs represent an important class of materials as they can exceed the stability and performance of electrochemical devices made with conventional, organic solvent-based electrolytes¹³. The main advantages that these materials offer are excellent physicochemical properties, i.e., thermal and electrochemical stability, high ionic conductivity, non-volatility and a high viscosity to suppress leakage. Consequently the developed materials provide additional prospects for other applications, which in this context can further foster the development of a holistic solution to a sustainable power production including gas treatment for fossil fired power plants and energy storage for renewable energy production.

An upscaling work has also been carried out on the salt additive, Zn(II)TFSI, which has led to increased production capacity, linked with substantial sales increase. In any case, the results obtained in the project provide **a framework for the synthesis of PIL/IL/salt additive formulations**, following the same strategy but using other PIL materials developed in the project (e.g. PILs prepared starting from commercially available polymer materials, such as cellulose acetate and poly(vinylbenzylchloride)), that can be applied for other applications. Additionally, the testing of PIL-based membrane technology for extended periods under “real-world” conditions has given valuable information on the real potential of this technology, similar to the other leading membrane technologies that are being evaluated. The INTERACT project has contributed in this sense, since literature data is scarce, and we have provided preliminary testing data. The membrane based on this PIL was selected for durability tests under realistic flue gas conditions (synthetic flue gas containing 15% CO₂ as well as minor contaminating components, such as O₂ and SO₂ in humidified conditions). As there was no negative impact observed on the membrane performance over this extended timeframe, the long-term temperature stability was investigated up to an operating temperature of 75 °C. An increase of CO₂ flux and decrease of CO₂/N₂ selectivity with increasing temperature was observed. Although the INTERACT project was focused on flue gas separation from coal fired power plants, the developed PIL-based membranes also proved their potential for other light gas separation, such as CO₂/CH₄ for biogas upgrading or natural gas refinery. PIL research has a very strong application focus driven by their functions which are not limited to separation applications. Some other emerging applications that have attracted the interest of the scientific community are: energy harvesting and storage (e.g. electrolyte materials for batteries) and catalysis (e.g. direct synthesis of cyclic carbonates via the coupling of CO₂ with epoxides).¹⁴

Innovative concepts for enzyme application in gas-liquid contacting systems

In the scope of the INTERACT project a full investigation of the **suitable operating ranges** in terms of pH, temperature and solvent concentrations have been performed for the investigated enzyme carbonic anhydrase, including dedicated long-term stability studies for various solvents. While the focus was placed on the application of an enzyme-solvent system for CO₂ separation in the context of a coal-fired power plant the results **can further be used to evaluate the application of the**

¹³ Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* 2009, 8, 621–629. B) Mecerreyes, D. *Prog. Polym. Sci.* 2011, 36, 1629–1648

¹⁴ Yuan et al.. *Progress in Polymer Science* **2013**, 38, 7, 1009-1036. “Poly(ionic liquid)s: An update”.

enzyme-solvent systems in other gas cleaning applications, based on the characterized operating ranges for each solvent system.

The characterization of the identified enzyme-solvent systems as well as several means for enzyme immobilization further demonstrated the potential improvement of the mass transfer rates towards an effective and energy-efficient CO₂ capture process, by means of enzymatic reactive absorption. In the course of the extensive experimental studies an **improvement of the measured CO₂ transfer by addition of the enzyme by a factor of up to 9** was determined for application in aqueous MDEA which is a well-known solvent in the gas scrubbing industry. Therefore, **adding enzyme directly overcomes the poor reaction kinetics of commercially important MDEA solvent** which allows for harvesting the beneficial properties of this kinetically limited tertiary amine, including lower heat of reaction and evaporation as well as a reduced corrosiveness when compared to primary amines such as MEA¹⁵. The investigations furthermore revealed that **the enzyme is capable of efficiently catalysing the reactive absorption even at reduced temperature**, extending the operating window towards higher gas solubility and therefore higher cyclic loadings, resulting in **further potential for a reduction in solvent requirements**. The transferability of the results obtained at lab scale and demonstration scale was further demonstrated by experimental investigations at pilot scale. The developed insight on enzyme accelerated solvent systems can further be transferred to innovative solvents offering even better thermodynamic properties than MDEA, taking into account blends of different molecules and computer aided molecular design tools.

The investigated means for **enzyme immobilization**, taking into account surface coating of magnetic nanoparticles or catalytic packings, the entrapment of enzyme beads inside the mesh-bags of catalytic packings and the innovative biocatalyst delivery system (BDS) provide a portfolio of different means for the implementation of enzymes in fluid separation processes in general and the results can be transferred to other applications, such as enzymatic reactive distillation for the production of bulk¹⁶ as well as fine chemicals and even chiral compounds¹⁷. Immobilization of the enzyme provides the possibility to control the conditions that are experienced by the enzyme and therefore adhere to the operating ranges for a stable enzyme application and extend the application ranges to further systems. In this respect, BDS particles worked very well, nearly matching dissolved enzyme performance. Other immobilization approaches resulted in a potential performance decrease that might be caused by a mere reduction of catalyst mass per volume, or could result from additional mass transfer limitation introduced by the solid form of immobilized enzymes, i.e. gas-liquid-solid interactions.

The results obtained for the application of enzyme activated solvents in membrane contactors additionally provide valuable insights that can be exploited for further evaluation of the technology in various CO₂ capture processes. Within the INTERACT project an **improvement of a ~36% increase in absorption rate was demonstrated by addition of PILs to the membrane surface** exposed to the gas side in the contactor. Such a hybrid membrane contactor concept provides additional prospect and triggers interest for further development of the idea using other routes in order to generate low cost, high flux membrane surfaces with high CO₂ affinity in order to increase the mass transport. Such membrane improvements would reduce the required amount of membrane surface area, making the technology cost-competitive and allowing for further investigations in forthcoming demonstration to pilot scale projects. The hybrid membrane contactor design concept is interesting not only for CO₂ capture but for other separations such as sulfur dioxide from various gas streams, methane / CO₂ and paraffin's/olefins in which the delivery of the desired

¹⁵ Yildirim et al., "Reactive absorption in chemical process industry: A review on current activities", Chem. Eng. J., 213, 2012

¹⁶ Wierschem et al., "Pilot-scale validation of Enzymatic Reactive Distillation for butyl butyrate production", Chem. Eng. J., 312 (2017), 106-117

¹⁷ Wierschem et al., "Evaluation of the Enzymatic Reactive Distillation for the Production of Chiral Compounds", Chem. Ing. Tech., 88 (2016), 147-157

product in a solvent stream is beneficial. It also opens up a further application for tailored PILs. In addition, other materials, which provide facilitated transport, could be considered for use in the hybrid membrane contactor.

Innovative energy and resource efficient process concepts for post combustion carbon capture

The strong decrease or elimination of CO₂ emissions from fossil fuelled power plants is a major target in the present and future environmental and political landscape. The necessity to reduce greenhouse gas emissions such as CO₂ by 80 to 95% before 2050 compared to 1990 has been proposed by the EU and reconfirmed by the European Council in February 2011. In order to succeed in this ambitious objective novel production processes and routes are required that allow the generation of targeted products and services with significantly reduced environmental footprints. Eventually being even more important, existing technologies need to be upgraded with technologies that limit the release of climate relevant emissions. With regard to post combustion capture the INTERACT project represents a breakthrough in the development of novel materials and techniques for the decarbonization of industrial CO₂ rich flue gases. Applying the materials and concepts developed on the application towards the flue gas stream of fossil fuelled power plants - which represent one of the main emitters of carbon dioxide - post combustion capture is performed in an energy- and cost-efficient way. Compared to today's standard MEA-based capture technology **a reduction of the expected energy penalty of the power plant of 29 % is predicated at substantially lower energy production costs (- 4 €/MWe) and CO₂-avoidance costs (- 6 €/tonCO₂)** as well as being more sustainable from a LCA perspective. In that sense the outcome of the INTERACT project can be considered a milestone concerning the European and global efforts of reducing carbon emissions up to 2050. Effective new materials embedded in novel process schemes have been designed. Exploiting these in industrial scenarios, economically attractive solutions for decarbonization of CO₂ rich flue gas streams have been identified that are technically feasible and robust to move to the next scale of demonstration. These solutions show the potential to pioneer efficient ways of environmentally friendly carbon dioxide sequestration and therefore can provide a crucial contribution to the future CCS efforts required to maintain a high quality of life.

The developed models, process concepts and methods provide the necessary foundation to efficiently evaluate the **application of the technologies to other gas cleaning processes, as e.g. in NGCC, IGCC, natural gas or biogas upgrading, or cement production**. The transfer of the developed methodologically approach to these additional applications requires merely an adaption of the problem specific parameters, accounting for feed and product specifications, cost and LCA data. Especially for the treatment of biogas and other scenarios with lower CO₂ capture rates process concepts such as the PIL-based gas membrane concepts, which were outperformed by the enzymatically catalysed reactive absorption process, provide a huge prospect. The developed methods present the necessary tools required to evaluate and optimize the various process concepts for these and other alternative applications. A **consecutive use developed conceptual design and process evaluation methods** and further development of the tools is already pursued in the context of a subsequent project named "NANOMEMC2-Projekt" ("NanoMaterials Enhanced Membranes for Carbon Capture", (<http://www.nanomemc2.eu/>), which is implemented in the context of Horizon 2020.

Impact on global market

The aim of the project was the development of new technologies for the CO₂ capture in various industries, for example in power plants. Although market share of coal, oil and gas fired power plants in Europe is decreasing, the number of fossil fuel powered power plants is increasing on the world

scale. In China alone there are about 693 coal fired power plants active¹⁸, while the US hold for another 380 coal fired power plants at the present time. Fossil fuel power plants are responsible for 45% of the worldwide emissions of greenhouse gases thus saving potential in this field is huge. Based on state-of-the art technology of packing vendors one 500 MW power plants requires absorption columns for CO₂ capture with a packing volume of ca. 10.000 m³, the unit price for packings used at the present time in ca. 200 €/m³, thus investment only in the packing is 2 million euro. With the use of novel enzymatic enhancers pressure drop can be reduced and capacity and mass transfer will be increased – this leads to smaller dimensions of the columns. The enhancement of mass transfer of 20% leads to savings only in packing investment of 400.000 €, not accounting for additional savings in smaller apparatus and construction. This leads to significant savings for the operators of the plant.

Energy requirements significantly benefit the use of bioreactive absorption over other technologies. According to Life Cycle studies, bioreactive absorption uses up to 250 kWh per ton recovered CO₂ compared to significantly higher values for pressure swing adsorption (1600-180 kWh), cryogenic distillation (600-800kWh) or amine absorption (330-340 kWh). Through the replacement of chemical absorption through enzyme enhanced CO₂ capture in which carbonic anhydrase (the enzyme responsible for CO₂ balance in the human body) is used we expect substantial reduction of inventory of toxic species in CO₂ capture processes

Technological impacts and risks

Despite the carved out large potential of the developed process concepts, especially the developed concept for an enzymatic-catalyzed reactive absorption process, further investigations are necessary to address remaining challenges for large-scale applications. Most of all further scale up demonstration of the technologies under commercially relevant conditions is required to address the transferability of the results in an industrial environment and to prove long-term stability and validate the cost-effectiveness of the developed process concepts. The research in the current project was devoted to the development of the new technologies. While the consortium tried to bridge the gap between material development, technology development and characterization and process design and evaluation, the core of the project was focused on the proof-of-concept of the developed technologies. By developing production processes that allows for an economic production of the developed materials (PILs and enzymes) and characterizing the developed technologies at lab- and demonstration scale the basis for further development to demonstration scale is set, and the developed process concepts already took into account issues related to further scale-up at a conceptual design level. The INTERACT consortium formed the ideal mix of partners for the pursued developments. Further progress in the direction of an industrial application requires appropriate industrial partners to implement and test the relevant technologies in an industrial environment and further develop the technology to suit the industrial requirements for a broad application.

European Transnational Approach

In order to develop the innovative materials and technologies for an economic and sustainable application of CO₂ capture in an industrial application scenario we need to strengthen the cooperation between European industry and research institutions. A very important impact of the INTERACT project was the close interactive nature of the consortium and frequent cross-work meaning that many researchers on the project gained exposure to new skills in applying the advanced technologies evaluated. This demystifies and mitigates risks further technology developments and builds up the labor force of, especially, young researchers, who are employable by industry and academia to further develop and implement the technologies. As many different factors play an

¹⁸ <http://www.live-counter.com/kohleverbrauch-weltweit/>

important role in energy production and power output of single power plants is introduced into a highly complex and strongly integrated multinational network, not only the cooperation between different countries, but also the integration into a holistic approach, considering carbon capture and storage or utilization for continuously operated fossil fired power plants as well as the discontinuously producing renewable energy production and the related energy storage, need consideration. This complex nationwide optimization problem can only be tackled efficiently if the overall efforts are strategically coordinated and the different technologies are put to the best possible use in an integrated and cooperative approach. Consequently, a European transnational approach provides the optimum platform for such coordinated developments to provide a more sustainable future throughout the European Union.

The realization of the current project has brought an improvement in terms of innovative and new materials, aiding the toolbox of different measures to provide more sustainable and economic solutions to reduce CO₂ emissions in the scope of power production but also other large-scale emitters, such as e.g. cement production. The knowledge accumulation in the involved research institutions will eventually result in new activities improving the developments in the different sectors and with time have a socially positive impact on the European Community. The involved industrial partner and SMEs in this project already benefitted from the novel developments and related markets that can improve their short and long term profits.

Use and dissemination of foreground

Section A – Dissemination measures, including any scientific publications relating to foreground

The project consortium is well aware of the fact that the dissemination as well as efficient exploitation of the project results are vital elements of the project success. Several dissemination activities have therefore been implemented to create awareness among the relevant stakeholder communities and to increase the visibility of the project and significant results. All activities were targeted to keep the stakeholder communities informed throughout the project, addressing various dissemination channels and diverse media.

The dissemination work was initiated with the design of a corporate identity, a project website and unified dissemination templates. The corporate identity was assured by a logo and standard promotional materials, such as flyers and general project descriptions, assuring a high degree of visibility of the project. Furthermore target groups were identified, as well as means for addressing these distinct groups, also keeping track of conferences and symposia specialised on CCS related topics.

All project partners were actively involved in the dissemination activities, taking efforts in their home country as well as internationally, to promote the outcome of the project in terms of

- General dissemination of the project activities directed to a broader public and
- Targeted dissemination of specific activities and outcomes to the identified target groups

For the direct dissemination of the project results to target groups an industrial advisory board was implemented with selected members from different representative industry sectors, including the energy sector, the chemical industry and technology providers. Besides the representation of the

project at several international events, including Australian-European and Korean-European workshops on CCS, a dedicated workshop on Innovative Materials and Technologies for CO₂ Capture was organized in which the latest project results were presented in combination with important results from industry and related European project on CCS.

All publications and presentations in the project were subject to a special release procedure to account for confidentiality issues.

The main stakeholder groups have been:

- **General public.** One of the goals of this project was create awareness for the importance of research addressing the global challenge of a sustainable future and specifically the reduction of greenhouse gas emissions in order to avoid an irreversible climate change. Main dissemination channels would be the project website, the implementation of a social media account, press releases, as well as articles for the general public and interviews.
- **Other projects.** The contact to and cooperation with other projects in the same or related calls is considered as a key factor in disseminating the project results to related and interested audience working on strongly related topics. Within the scope of several internationally linked workshops direct contact with the FP7 projects ASCENT, Green-CC, HiperCap, Matesa and M4CO₂, as well as CAPSOL has been established and project results have been presented with these projects at joint workshops at Australian and Korean CCS workshops. The aim has been an exchange of the project outcomes for a maximization of the impact and multiplication of the audience.
- **Relevant associations.** In order to disseminate the results to a broader audience in the related research and industrial application fields the communication of project events was fostered by referring to the project and project events in newsletters of relevant associations, such as SPIRE or the CCS Association.
- **Research communities.** One of the major objectives was of course the distribution of the results to research communities working on CCS and related research fields. By a direct communication of the recent research results the influence of the project on the current developments in the field can be maximized. Therefore all relevant communication channels, especially national expert comity meetings and international conferences and workshops have been strongly addressed and the results have been and are currently still in the process of being published in well-recognized peer-reviewed scientific journals.
- **Industrial end-users.** Industrial end-users are of course the most relevant group to address a direct transfer of the research results into industrial application. The main dissemination channels to reach this group were dedicated events and workshops, specifically the final project workshop, to which a wide range of industrial end-users from the power sector, the chemical industry and technology providers were invited. Besides these a representative industrial advisory board was implemented to provide feedback from the end-user perspective and advice on the dissemination of the results.

After the end of the project, there still will be several publications issued by the involved individual partners. The consortium agreed to keep the release procedure for at least one year after the project is finished.

The website www.interact-co2.eu will be kept online for at least 2 years after the project end.

Section B – Exploitable foreground and the plans for exploitation

An important factor of the exploitation of the project results is the potential utilization in further research projects, as well as the commercialization of the developments that have been made in the scope of the project. In order to foster these activities a detailed plan for exploitation has been made and repeatedly updated in the course of the project. All partners were involved in the process of generating, updating and finalizing the plan for exploitation, providing a list of exploitable items, ranging from the synthesis strategies and production scale-up strategies of PILs, up to the developed process concepts on the basis of the different technologies and their implementation. As some of the technologies have till now been developed on a proof-of-concept basis, additional efforts are required to demonstrate an industrial validation under according conditions.

Since the project results are not restricted to the invention of the new technologies for efficient CO₂ capture from power plant flue gas, adjacent applications, such as cement flue gas and biogas treatment provide further potential for the exploitation of the developed technologies. For example, applying the developed technologies to biogas upgrading to produce Renewable Natural Gas (RNG) could align very well with the push for more sustainable transportation fuels. . The potential to implement the developed technologies for production of RNG is excellent in Europe, where relatively large biogas infrastructure already exists. Moreover, RNG is a “drop in” fuel that can be used also as a diesel replacer for shipping and high horsepower vehicles where few low carbon alternatives exist. This could thus very well fit in future EC low carbon initiatives. The developed materials, especially the various types of PILs, as well as the synthesis techniques and the proven production methods at larger scale allow for an exploitation of the results even outside the considered gas cleaning application.

In order to allow for the exploitation of the results of the project by the partners as well as third parties, the results are thoroughly described and documented by the coordinator, based on the contributions from the work package leaders involved in the project. Data that is deemed commercially sensitive and whose accessibility should be limited to the Commission officials only is clearly indicated. The documentation was subject to distinct updates whenever a significant development target or a milestone within the project was accomplished. The procedure was overseen by the exploitation panel within the project.

The results (deliverables, flash reports, periodic reports) were made available to all partners without any restriction for internal use.

Patent applications were to be filed for products that can be commercialised directly, if relevant. Companies outside the consortium were and are to be addressed in case they seem more suitable for this purpose than any consortium partner.

Section A (public)

This section includes two templates

- Template A1: List of all scientific (peer reviewed) publications relating to the foreground of the project.
- Template A2: List of all dissemination activities (publications, conferences, workshops, web sites/applications, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters).

These tables are cumulative, which means that they should always show all publications and activities from the beginning until after the end of the project. Updates are possible at any time.

TEMPLATE A1: LIST OF SCIENTIFIC (PEER REVIEWED) PUBLICATIONS, STARTING WITH THE MOST IMPORTANT ONES										
NO.	Title	Main author	Title of the periodic al or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers ¹⁹ (if available)	Is/Will open access ²⁰ provided to this publication?
1	<i>Enzymatically Assisted CO₂ Removal from Flue-gas</i>	<i>Maria T. Gundersen , Nicolas von Solms , John M. Woodley</i>	<i>Energy Procedia</i>	<i>Vol. 63</i>	<i>Elsevier BV</i>	<i>Netherlands</i>	<i>2014</i>	<i>pp. 624-632</i>	<i>10.1016/j.egypro.2014.11.067</i>	<i>yes</i>
2	<i>Facile and Scalable Synthesis of Nanoporous Materials Based on Poly(ionic liquid)s</i>	<i>Itxaso Azcune , Ignacio García , Pedro M. Carrasco , Aratz Genua , Marek Tanczyk , Manfred Jaschik , Krzysztof Warmuzinski , Germán Cabañero ,</i>	<i>ChemSus Chem</i>	<i>Vol. 7/Issue 12</i>	<i>Wiley-VCH Verlag</i>	<i>Germany</i>	<i>2014</i>	<i>pp. 3407-3412</i>	<i>10.1002/cssc.201402593</i>	<i>no</i>

¹⁹ A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

²⁰ Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

		Ibon Odriozola								
3	Reactive absorption of CO ₂ into enzyme accelerated solvents: From laboratory to pilot scale	Anna-Katharina Kunze , Greg Dojchinov , Victoria S. Haritos , Philip Lutze	Applied Energy	Vol. 156	Elsevier BV	Netherlands	2015	pp. 676-685	10.1016/j.apenergy.2015.07.033	yes
4	Conceptual Design of Post-Combustion CO ₂ Capture Processes - Packed Columns and Membrane Technologies	Mathias Leimbrink , Anna-Katharina Kunze , David Hellman, Andrzej Górak, Mirko Skiborowski	Computer Aided Chemical Engineering	Vol. 37	Elsevier	Netherlands	2015	1223-1228	10.1016/B978-0-444-63577-8.50049-8	No
5	Influence of temperature and solvent concentration on the kinetics of the enzyme carbonic anhydrase in carbon capture technology	Arne Gladis , Maria T. Gundersen , Philip L. Fosbøl , John M. Woodley , Nicolas von Solms	Chemical Engineering Journal	Vol. 309	Elsevier	Netherlands	2017	pp. 772-786	10.1016/j.cej.2016.10.056	yes
6	Different strategies for accelerated CO ₂ absorption in packed columns by application of the biocatalyst carbonic anhydrase	Mathias Leimbrink, Timo Limberg, Anna-Katharina Kunze, Mirko Skiborowski	Energy Procedia		Elsevier BV	Netherlands	2017		10.1016/j.egypro.2017.03.1221 DOI available, but not yet uploadable in SESAM	
7	Enzyme accelerated carbon capture in different contacting equipment - a comparative study	Mathias Leimbrink, Kolja Neumann, Katharina Kupitz, Andrzej Górak, Mirko Skiborowski	Energy Procedia		Elsevier BV	Netherlands	2017		10.1016/j.egypro.2017.03.1222 DOI available, but not yet uploadable in SESAM	
8	Transport and separation of carbon dioxide and nitrogen in a novel composite poly(ionic liquid)/ionic liquid/Zn[NTf ₂] ₂	M. Tanczyk, M. Jaschik, J. Jaschik, K. Warmuzinski, R. Lin, S. Fantini, F. Malbosc and S. Loïs	Journal of Membrane Science		Elsevier	Netherlands	Submitted			
9	Enzymatic reactive absorption of CO ₂ in MDEA by meand of an innovative biocatalyst delivery system	Mathias Leimbrink, Klaudia Grazyna Nikoleit, Rüdiger Spitzer, Sonja Salmon, Tracy Bucholz, Andrzej Górak, Mirko Skiborowski	Chemical Engineering Journal				Submitted			

10	<i>Pilot Scale Testing and Modeling of Enzymatic Reactive Absorption in Packed Columns for CO₂ Capture</i>	Mathias Leimbrink, Stepgen Tlatlik, Sonja Salmon, Anna-Katharina Kunze, Timo Limberg, Rüdiger Spitzer, Axel Gottschalk, Andrzej Górak, Mirko Skiborowski	<i>Int. J. Greenhouse Gas Control (column 47)</i>		<i>Elsevier</i>	<i>Netherlands</i>	2017		10.1016/j.ijggc.2017.04.010	
11	<i>Enzyme carbonic anhydrase accelerated CO₂ absorption in membrane contactor</i>	Edel Sheridan, Taek-Joong Kim, Alexander Lang, Actor Chikukwa, Paul Inge Dahl, Mathias Leimbrink, Johannes Roubroeks	<i>Energy Procedia</i>		<i>Elsevier BV</i>	<i>Netherlands</i>	2017		10.1016/j.egypro.2017.03.1141 DOI available, but not yet uploadable in SESAM	
12	<i>Post-synthetic modification of conventional polymers: a pathway to facile poly(ionic liquids) for CO₂ capture</i>	Daria Nikolaeva, Edel Sheridan, Marius Sandru, Itxaso Azcune, Aratz Genua, Manfred Jaschik, Krzysztof Warmuzinski and Ivo J.F. Vankelecom	<i>RSC Green Chemistry</i>				submitted			
13	<i>CO₂ mass transfer model for carbonic anhydrase enhanced MDEA solutions</i>	Arne Gladis, Maria Gundersen Deslauriers, Neerup R., Fosbøl, P. L., John Woodley, Nicolas von Solms	<i>Chemical Engineering Journal</i>				submitted			
14	<i>Enzymatic Reactive Absorption and Distillation</i>	Matthias Wierschem, Mathias Leimbrink, Mirko Skiborowski, Rene Heils, Irina Smirnova, Andrzej Górak	<i>Intensification of Bio-Based Processes</i>				Submitted to RSC Green Chemistry			
15	<i>Different strategies for accelerated CO₂ absorption in packed columns by application of the biocatalyst carbonic anhydrase</i>	Mathias Leimbrink, Timo Limberg, Anna-Katharina Kunze, Mirko Skiborowski	<i>Energy Procedia</i>				accepted			

16	<i>Operating considerations of ultrafiltration in enzyme enhanced carbon capture</i>	<i>Maria Gundersen Deslauriers, Arne Gladis, Fosbøl, P. L., Nicolas von Solms, John Woodley</i>	<i>Energy Procedia</i>				<i>accepted</i>			
17	<i>Pilot absorption experiments with carbonic anhydrase enhanced MDEA</i>	<i>Arne Gladis, Niels F. Lomholt, Fosbøl, P. L., John Woodley, Nicolas von Solms</i>	<i>Energy Procedia</i>				<i>accepted</i>		<i>10.1016/j.egypro.2017.03.1278</i> <i>DOI available, but not yet uploadable in SESAM</i>	
18	<i>Comparison of the kinetic promoters piperazine and carbonic anhydrase for CO₂ absorption</i>	<i>Arne Gladis, Niels F. Lomholt, Fosbøl, P. L., John Woodley, Nicolas von Solms</i>	<i>Energy Procedia</i>				<i>accepted</i>		<i>10.1016/j.egypro.2017.03.1214</i> <i>DOI available, but not yet uploadable in SESAM</i>	

TEMPLATE A2: LIST OF DISSEMINATION ACTIVITIES								
NO.	Type of activities ²¹	Main leader	Title	Date/Period	Place	Type of audience ²²	Size of audience	Countries addressed
1	<i>Presentation at conference</i>	<i>SUPREN</i>	<i>R&D on InnovaTive Enzymes and polyionic-liquids based membRAnes as post combustion CO₂ Capture key Technology</i>	<i>08.10.2013</i>	<i>Essen, Germany</i>	<i>Scientific community and industry</i>		<i>EU</i>

²¹ A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, Other.

²² A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias, Other ('multiple choices' is possible).

2	Project website	TUDO	http://interact-co2.eu/	30.11.2013	Dortmund, Germany	Scientific community, industry, Civil Society, Policy makers and Medias	n/s	Worldwide
3	University Publication/Scientific Monograph	DTU	Evaluating Enzymatically Assisted CO ₂ Removal from Flue-Gas with Carbonic Anhydrase	11.12.2013	Lyngby, Denmark	Scientific community		EU
4	Poster at conference	DTU	CO ₂ capture using enzyme-enhanced solvents	25.07-27.07.2014	Lyngby, Denmark	Scientific community and industry		EU
5	Poster at conference	DTU	Enzymatically Assisted CO ₂ Removal from Flue-Gas	25.07-27.07.2014	Lyngby, Denmark	Scientific community and industry		EU
6	Presentation at conference	TUDO	Biocatalysts for enhanced CO ₂ postcombustion capture efficiency in absorption columns	16.09.2014	Friedrichshafen, Germany	Scientific community and industry	50	EU
7	Poster at conference	DTU	Enzymatically Assisted CO ₂ Removal from Flue-Gas	05-10.-09.10.2014	Austin, TX, USA	Scientific community and industry		Worldwide
8	University Publication/Scientific Monograph	DTU	Evaluating Enzymatically Assisted CO ₂ Removal from Flue-Gas with Carbonic Anhydrase	24.11.2014	Lyngby, Denmark	Scientific community		EU
9	University Publication/Scientific Monograph	DTU	Enzyme enhanced carbon dioxide absorption	24.11.2014	Lyngby, Denmark	Scientific community		EU
10	Poster and conference Paper	TUDO	Conceptual Design of Post-Combustion CO ₂ Capture Processes - Packed Columns and Membrane Technologies	31.05-04.06.2015	Copenhagen, Denmark	Scientific community and industry	1000	EU
11	Presentation at conference	DTU	Reaction enhancement of post-combustion carbon capture using carbonic anhydrase	16.06-18.06.2015	Trondheim, Norway	Scientific community and industry	700	EU
12	Poster at conference	DTU	Carbon dioxide	17.06.2015	Trondheim, Norway	Scientific	700	EU

			<i>absorption rate intensification by carbonic anhydrase for different solvent types</i>			<i>community and industry</i>		
13	<i>Poster at conference</i>	SINTEF	<i>Novel CO₂ capture membranes based on polymerized ionic liquids and polymeric porous supports</i>	17.06.2015	Trondheim, Norway	<i>Scientific community and industry</i>	700	EU
14	<i>Presentation at conference</i>	TUDO	<i>Investigation of an Intensified CO₂ Capture Process –Reactive and Enzymatic Capture in Membrane Contactors</i>	17.06.2015	Trondheim, Norway	<i>Scientific community and industry</i>	700	EU
15	<i>Abstract and presentation at conference</i>	KULEU	<i>Poly(ionic liquid)s-based thin film composite membranes to enhance process stability in CO₂ capture applications.</i>	01.09.2015-10.09.2015	Aachen, Germany	<i>Scientific community and industry</i>	400	EU
16	<i>Presentation at conference</i>	TUDO	<i>Process intensification of CO₂ capture by means of membrane contactors and efficient biocatalysts</i>	08.09.2015	Aachen, Germany	<i>Scientific community and industry</i>	400	EU
17	<i>Abstract</i>	DTU	<i>Reaction kinetics of the enzyme Carbonic Anhydrase in promoted chemical solvents for carbon dioxide absorption</i>	08.09.2015-11.09.2015	Regina, Canada	<i>Scientific community and industry</i>	200	Worldwide
18	<i>Abstract</i>	DTU	<i>Technical evaluation of implementation of carbonic anhydrase in post-combustion carbon capture</i>	08.09.2015-11.09.2015	Regina, Canada	<i>Scientific community and industry</i>	200	Worldwide
19	<i>Presentation at workshop</i>	KULEU	<i>Poly(ionic liquid)s-based thin film composite membranes to enhance process stability in CO₂ capture applications</i>	1-3.10.2015	Rende, Italy	<i>Scientific community and industry</i>		EU
20	<i>Midterm workshop</i>	KULEU	<i>INTERACT midterm workshop</i>	17.11.2015	Leuven, Belgium	<i>Scientific Community, Industry</i>	23 participants	EU

21	Presentation at conference	DTU	How to use carbonic anhydrase enzyme in carbon capture technology	31.08.2016	Prague, Czech Republic	Scientific community and industry		EU
22	Presentation at conference	TUDO	Effiziente CO ₂ Abtrennung durch enzymatische Reaktivabsorption	12.09.-15.09.2016	Aachen, Germany	Scientific community and industry	400	EU
23	Presentation at conference	SINTEF	Novel CO ₂ capture membranes based on polymerized ionic liquids and polymeric porous supports	11.09-16.09.2016	Cork, Ireland	Scientific community and industry		EU
24	Poster at conference	SINTEF	Accelerated CO ₂ absorption in a membrane contactor using enzyme carbonic anhydrase	11.09-16.09.2016	Cork, Ireland	Scientific community and industry		EU
25	Presentation at a workshop	KULEU	Poly(ionic liquids) by post-modification synthesis: pathway to polymer optimisation	3.10.2016-4.10.2016	Lisbon, Portugal	Scientific community and industry		EU
26	Presentation at conference	DTU	Carbonic Anhydrase Enhanced Carbon Capture: Kinetic Measurements and Pilot Plant Trials	13.11.2016-18.11.2016	San Francisco, USA	Scientific community and industry	1000	Worldwide
27	Presentation at conference	TUDO	Improving the energy efficiency of carbon capture processes – Combining enzyme accelerated solvent systems and improved contacting equipment	13.11.2016-18.11.2016	San Francisco, USA	Scientific community and industry	1000	Worldwide
28	Conference paper and poster	SINTEF	Enzyme carbonic anhydrase accelerated CO ₂ absorption in membrane contactor	14.11.-18.11.2016	Lausanne, Switzerland	Scientific community and industry	1000	EU
29	Conference paper and poster	TUDO	Different strategies for accelerated CO ₂ absorption in packed columns by application	14.11.-18.11.2016	Lausanne, Switzerland	Scientific community and industry	1000	EU

			<i>of the biocatalyst carbonic anhydrase</i>					
30	Conference paper and poster	TUDO	Enzyme accelerated carbon capture in different contacting equipment - a comparative study	14.11.-18.11.2016	Lausanne, Switzerland	Scientific community and industry	1000	EU
31	Conference paper	DTU	Operating considerations of ultrafiltration in enzyme enhanced carbon capture	14.11.-18.11.2016	Lausanne, Switzerland	Scientific community and industry	1000	EU
32	Presentation at conference	TUDO	Project presentation INTERACT	14.11.-18.11.2016	Lausanne, Switzerland	Scientific community and industry	1000	EU
33	poster and conference paper	DTU	Pilot absorption experiments with carbonic anhydrase enhanced MDEA	14.11.-18.11.2016	Lausanne, Switzerland	Scientific community and industry	1000	EU
34	Conference paper	DTU	Comparison of the kinetic promoters piperazine and carbonic anhydrase for CO ₂ absorption	14.11.-18.11.2016	Lausanne, Switzerland	Scientific community and industry	1000	EU
35	University Publication/Scientific Monograph	DTU	Design of Biocatalytic Processes	16.11.2016	Lyngby, Denmark	Scientific community		EU
36	Final workshop with potential end-users	TUDO	INTERACT final workshop	12.01.2017	Leverkusen, Germany	Scientific Community, Industry	43 participants	11 European countries as well as the US and Australia
37	Flyer final workshop	TUDO	INTERACT final workshop flyer	12.01.2017	Leverkusen, Germany	Scientific Community, Industry	43 participants	11 European countries as well as the US and Australia
38	Presentation and conference paper	TUDO	Membrankontaktoren - Breitflächig anwendbare Option zur Prozessintensivierung oder Nischenlösung?	09.02.2017	Kassel, Germany	Scientific community and industry	100	EU

39	<i>Presentation at conference</i>	<i>TUDO</i>	<i>Enzymatische Reaktivabsorption trifft intensivierte Fluidverfahrenstechnik</i>	<i>09.03.2017</i>	<i>Cologne, Germany</i>	<i>Scientific community and industry</i>	<i>300</i>	<i>EU</i>
40	<i>Poster at the summer school</i>	<i>KULEU</i>	<i>Cellulose acetate-based poly(ionic liquids) as a pathway to facile membranes for CO₂ capture from biogas</i>	<i>26.06.2017- 30.06.2017</i>	<i>Lund, Sweden</i>	<i>Scientific community and industry</i>		<i>EU</i>
41	<i>Poster at the conference</i>	<i>KULEU</i>	<i>Polyvinylbenzyl chloride- based polymers as a pathway to facile poly(ionic liquids) for CO₂ capture</i>	<i>29.07.2017- 4.08.2017</i>	<i>San Francisco, USA</i>	<i>Scientific community and industry</i>		<i>Worldwide</i>
42	<i>Project flyer</i>	<i>TUDO</i>	<i>INTERACT project flyer</i>		<i>Dortmund, Germany</i>	<i>Scientific community and industry</i>	<i>n/s</i>	<i>Worldwide</i>

Section B (Confidential²³ or public: confidential information to be marked clearly)
Part B1

The applications for patents, trademarks, registered designs, etc. shall be listed according to the template B1 provided hereafter.

The list should, specify at least one unique identifier e.g. European Patent application reference. For patent applications, only if applicable, contributions to standards should be specified. This table is cumulative, which means that it should always show all applications from the beginning until after the end of the project.

TEMPLATE B1: LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights ²⁴ :	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
Patent	Yes	31/10/2017	<i>in progress</i>	Cellulose acetate derived PIL, as a new membrane material	Ivo Vankelecom, Itxaso Azcune, Daria Nikolaeva

²³ Note to be confused with the "EU CONFIDENTIAL" classification for some security research projects.

²⁴ A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.

Part B2

Please complete the table hereafter:

Type of Exploitable Foreground ²⁵	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ²⁶	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
Commercial exploitation of R&D results	New enzymatic packing as internal for column operation	NO		Stable enzymatic packing	Fine chemical production, chemical processing and pharma industry	>2016	Surface modification and in structured packing may be covered by patents	TUDO, DTU and Novozymes
Commercial exploitation of R&D results	Decreased desorption energy with enzyme/ enzyme benefit in desorption	NO		Enzyme in desorber (e.g. column, tank, or membrane type) reduces energy penalty for desorption	CO2 capturing industries	>2018	Take into consideration patent application WO201205503 5	TUDO, DTU, SINTEF, Novozymes
General advancement of knowledge	Hybrid configurations between column and contactors for CO2 removal			New CO2 process	Energy and chemical industry	>2017	None	TUDO, SINTEF, SUPREN
General advancement of knowledge	Improved flow characteristics in membrane			Optimized module for better flow	All kinds in which membrane	>2017	Some patents but freedom to operate still	PRODINTEC, TUDO

¹⁹ A drop down list allows choosing the type of foreground: General advancement of knowledge, Commercial exploitation of R&D results, Exploitation of R&D results via standards, exploitation of results through EU policies, exploitation of results through (social) innovation.

²⁶ A drop down list allows choosing the type sector (NACE nomenclature) : http://ec.europa.eu/competition/mergers/cases/index/nace_all.html

Type of Exploitable Foreground ²⁵	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ²⁶	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
	<i>contactors using model-based approaches</i>			<i>characteristics in membrane contactors</i>	<i>apparatuses are in use</i>		<i>possible</i>	
General advancement of knowledge	<i>Detailed models for reactive separation processes</i>			<i>Design and Optimization method</i>	<i>Fine chemical production, chemical processing and pharma industry</i>	<i>>2017</i>	<i>None</i>	<i>TUDO</i>
General advancement of knowledge	<i>Efficient Solvent/membrane contactor system</i>			<i>New CO2 process</i>	<i>Energy and chemical industry</i>	<i>>2017</i>	<i>None</i>	<i>TUDO, SINTEF, SUPREN</i>
<i>Commercial exploitation of R&D results</i>	<i>Efficient Solvent and enzyme system</i>	<i>NO</i>		<i>New CO2 process</i>	<i>Energy and chemical industry</i>	<i>>2017</i>	<i>None</i>	<i>Novozymes, TUDO, DTU</i>
General advancement of knowledge	<i>Techniques for deriving mass transfer coefficients for absorption/desorption</i>			<i>Standardized method for measuring and distinguishing mass transfer coefficients</i>	<i>Fine chemical production, chemical processing and pharma industry, Energy sector</i>	<i>>2016</i>	<i>None</i>	<i>DTU, TUDO</i>
General advancement	<i>Development of PILs and criteria for</i>	<i>NO</i>		<i>Targeted Membranes</i>	<i>Fine chemical production, chemical</i>	<i>>2017</i>	<i>None</i>	<i>CIDETEC, KULEU, SOLVIONIC</i>

Type of Exploitable Foreground ²⁵	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ²⁶	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
of knowledge	<i>systematic selection of IL</i>				<i>processing and pharma industry, Energy sector</i>			<i>ICEPAS</i>
General advancement of knowledge	<i>Temperature control strategies for absorption/desorption</i>			<i>New process and/or new technique for absorption/desorption</i>	<i>Fine chemical production, chemical processing and pharma industry, Energy sector</i>	<i>>2017</i>	<i>None</i>	<i>TUDO, SUPREN</i>
General advancement of knowledge	<i>Membrane contactor experimental techniques</i>			<i>Standardized method for comparable membrane contactor experiments</i>	<i>Chemical processing, food and pharma industry</i>	<i>>2016</i>	<i>None</i>	<i>TUDO + Sintef</i>
General advancement of knowledge	<i>Capture Short-Cut method</i>			<i>Method to determine the most economical technology(ies) and operating conditions for a required capture efficiency (separation task)</i>	<i>Chemical processing, food and pharma industry</i>	<i>>2016</i>	<i>None</i>	<i>TUDO</i>

Type of Exploitable Foreground ²⁵	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ²⁶	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
Commercial exploitation of R&D results	Identification of follow-up projects			Identification of follow-up projects and relevant industries for patent licensing and further joint development	Fine chemical production, chemical processing and pharma industry, Energy sector	>2016	None	SUPREN
Commercial exploitation of R&D results	Identification of follow-up projects			Identification of follow-up projects and relevant industries for patent licensing and further joint development	Fine chemical production, chemical processing and pharma industry, Energy sector	Continuous	None	All partners
Commercial exploitation of R&D results	Absorption with hybrid membrane contactor system with PILs and enzyme activated solvents			New process for CO2 absorption with membrane contactor application	Energy and chemical industry	>2017	Possibility to patent evaluated, use of enzymes is well covered, use of ILs in/as solvent is also covered, but not the combination of PILs layers and enzymes.	SINTEF, TUDO, Novozymes
Commercial exploitation of	Desorption with hybrid			New CO2	Energy and	>2017		SINTEF,

Type of Exploitable Foreground ²⁵	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ²⁶	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
<i>R&D results</i>	<i>membrane contactor system with PILs and enzyme activated solvents</i>			<i>desorption process</i>	<i>chemical industry</i>			<i>TUDO, Novozymes</i>
General advancement of knowledge	<i>Desorption with membrane contactor and reduced pressure</i>			<i>New/modified process for CO2 desorption</i>	<i>Energy and chemical industry</i>	<i>>2017</i>	<i>Patent possibilities under investigation</i>	<i>SINTEF</i>
General advancement of knowledge	<i>Performance of gas separation membranes with CO2/methane mixtures</i>	<i>NO</i>		<i>New application of developed membranes for natural gas (methane) sweetening</i>	<i>Energy and chemical industry</i>	<i>>2017</i>	<i>None</i>	<i>KULEU, CIDETEC, SINTEF</i>
General advancement of knowledge	<i>Concept of hybrid membrane contactor system with selective (PIL within INTERACT) layers</i>			<i>Unique membrane architecture: Functionalization of gas side of membrane to increase CO2 affinity</i>	<i>Energy and chemical industry</i>	<i>>2017</i>	<i>None</i>	<i>SINTEF, TUDO</i>

Type of Exploitable Foreground ²⁵	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ²⁶	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
General advancement of knowledge	Concept of hybrid membrane contactor system with selective (PIL within INTERACT) layers	NO		Unique membrane architecture: Functionalization of membrane to increase affinity towards other components	Energy and chemical industry where other separation processes besides CO2 is relevant (gas-liquid, liquid-gas and liquid-liquid contactors) e.g. biogas/biofuels	>2017	None	SINTEF
General advancement of knowledge	Techniques for deriving permeability coefficients in membrane materials from gravimetric measurements	NO		Standardized method for determining permeability coefficients	Fine chemical production, chemical processing and pharmaceutical industry, Energy sector	>2017	None	ICE-PAS, CIDETEC, SOLVIONIC
General advancement of knowledge	Numerical simulators for adsorptive and	NO		New CO2-capture process	Power and chemical industry	>2017	none	ICE-PAS, CIDETEC, SOLVIONIC, KULEU, SINTEF

Type of Exploitable Foreground ²⁵	Description of exploitable foreground	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application ²⁶	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
	<i>membrane processes</i>							
General advancement of knowledge	<i>Cellulose acetate derived PIL, as a new membrane material</i>			<i>FUJIFILM has shown interest to test cellulose acetate derived PIL for their co2 separation process</i>	<i>CO2 separation membrane</i>	<i>>2017</i>	<i>It is a new material, if the material performance is suitable for FUJIFILM, IPR protection is feasible.</i>	<i>KULEUVEN CIDETEC</i>
Commercial exploitation of R&D results	<i>3D printing of micro-porous structures</i>			<i>New parameters for additive manufacturing of micro-porous structures</i>	<i>Industry in general</i>	<i>Industry in general</i>	<i>None</i>	<i>PRODINTEC</i>
Commercial exploitation of R&D results	<i>Scale-up of POLYDDA TFSI synthesis process</i>	<i>YES</i>		<i>Commercialisation of the product</i>	<i>Electrochemical Energy storage systems</i>	<i>Started on 2015</i>	<i>Non applicable</i>	<i>Solvionic</i>
Commercial exploitation of R&D results	<i>Scale-up of Zn(II)TFSI synthesis process</i>	<i>YES</i>		<i>Commercialisation of the product</i>	<i>Electrochemical Energy storage systems</i>	<i>Increase production capacity</i>	<i>Non applicable</i>	<i>Solvionic</i>

In addition to the table, please provide a text to explain the exploitable foreground, in particular:

- Its purpose: development of upscaled process for one of the membrane components (polyDDATFSI)
- How the foreground might be exploited, when and by whom: already commercialised since 2015 by Solvionic

- IPR exploitable measures taken or intended: protection of know-how (confidentiality measures)
- Further research necessary, if any: improvement of the polymer properties for specific applications and markets

Potential/expected impact (quantify where possible): from 2014 (first market introduction to 2016), the turnover related to this product has increased by 6. Further increase by 3 to for is expected in 2017 versus 2016

Report on societal implications

Replies to the following questions will assist the Commission to obtain statistics and indicators on societal and socio-economic issues addressed by projects. The questions are arranged in a number of key themes. As well as producing certain statistics, the replies will also help identify those projects that have shown a real engagement with wider societal issues, and thereby identify interesting approaches to these issues and best practices. The replies for individual projects will not be made public.

A General Information *(completed automatically when Grant Agreement number is entered.*

Grant Agreement Number:

608535

Title of Project:

INnovaTive Enzymes and polyionic liquids based membRAnes

Name and Title of Coordinator:

Prof. Dr.-Ing. Andrzej Górak, TU Dortmund

B Ethics

1. Did your project undergo an Ethics Review (and/or Screening)?

- If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final project reports?

No

Special Reminder: the progress of compliance with the Ethics Review/Screening Requirements should be described in the Period/Final Project Reports under the Section 3.2.2 'Work Progress and Achievements'

2. Please indicate whether your project involved any of the following issues (tick box) :

RESEARCH ON HUMANS

- Did the project involve children?
- Did the project involve patients?
- Did the project involve persons not able to give consent?
- Did the project involve adult healthy volunteers?
- Did the project involve Human genetic material?
- Did the project involve Human biological samples?
- Did the project involve Human data collection?

RESEARCH ON HUMAN EMBRYO/FOETUS

- Did the project involve Human Embryos?
- Did the project involve Human Foetal Tissue / Cells?
- Did the project involve Human Embryonic Stem Cells (hESCs)?
- Did the project on human Embryonic Stem Cells involve cells in culture?
- Did the project on human Embryonic Stem Cells involve the derivation of cells from Embryos?

PRIVACY

- Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?
- Did the project involve tracking the location or observation of people?

RESEARCH ON ANIMALS

- Did the project involve research on animals?
- Were those animals transgenic small laboratory animals?
- Were those animals transgenic farm animals?

• Were those animals cloned farm animals?	
• Were those animals non-human primates?	
RESEARCH INVOLVING DEVELOPING COUNTRIES	
• Did the project involve the use of local resources (genetic, animal, plant etc)?	
• Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	
DUAL USE	
• Research having direct military use	No
• Research having the potential for terrorist abuse	

C Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator	0	4
Work package leaders	4	4
Experienced researchers (i.e. PhD holders)	19	41
PhD Students	1	4
Other	24	22

4. How many additional researchers (in companies and universities) were recruited specifically for this project? **2**

Of which, indicate the number of men: **1**

D Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project? ☒ Yes ☐ No

6. Which of the following actions did you carry out and how effective were they?

		Not at all effective			Very effective
☐	Design and implement an equal opportunity policy	☐	☐	☐	☐
☐	Set targets to achieve a gender balance in the workforce	☐	☐	☐	☐
☐	Organise conferences and workshops on gender	☐	☐	☐	☐
☐	Actions to improve work-life balance	☐	☐	☐	☐
☐	Other:				

7. Was there a gender dimension associated with the research content – i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?

☐ Yes- please specify

☒ No

E Synergies with Science Education

8. Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?

☐ Yes- please specify

☒ No

9. Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?

☐ Yes- please specify

☒ No

F Interdisciplinarity

10. Which disciplines (see list below) are involved in your project?

☒ Main discipline²⁷: 2.3

☐ Associated discipline²⁷:

☐ Associated discipline²⁷:

G Engaging with Civil society and policy makers

11a Did your project engage with societal actors beyond the research community? (if 'No', go to Question 14)

☒

Yes

☐

No

11b If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?

☐ No

☐ Yes- in determining what research should be performed

☐ Yes - in implementing the research

☒ Yes, in communicating /disseminating / using the results of the project

²⁷ Insert number from list below (Frascati Manual).

11c In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?	☒ x	☐ Yes ☐ No
12. Did you engage with government / public bodies or policy makers (including international organisations)		
☐ No ☐ Yes- in framing the research agenda ☐ Yes - in implementing the research agenda ☒ Yes, in communicating /disseminating / using the results of the project		
13a Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?		
☒ Yes – as a primary objective (please indicate areas below- multiple answers possible) ☐ Yes – as a secondary objective (please indicate areas below - multiple answer possible) ☐ No		
13b If Yes, in which fields?		
Agriculture Audiovisual and Media Budget Competition Consumers Culture Customs Development Economic and Monetary Affairs Education, Training, Youth Employment and Social Affairs	X X	Energy Enlargement Enterprise Environment External Relations External Trade Fisheries and Maritime Affairs Food Safety Foreign and Security Policy Fraud Humanitarian aid
		X x
		Human rights Information Society Institutional affairs Internal Market Justice, freedom and security Public Health Regional Policy Research and Innovation Space Taxation Transport
		x

13c If Yes, at which level? ☐ Local / regional levels ☐ National level ☒ European level ☒ International level		
H Use and dissemination		
14. How many Articles were published/accepted for publication in peer-reviewed journals?		43
To how many of these is open access²⁸ provided?		5
How many of these are published in open access journals?		2
How many of these are published in open repositories?		0
To how many of these is open access not provided?		2
Please check all applicable reasons for not providing open access:		
☐ publisher's licensing agreement would not permit publishing in a repository ☐ no suitable repository available ☐ no suitable open access journal available ☐ no funds available to publish in an open access journal ☐ lack of time and resources ☐ lack of information on open access ☐ other ²⁹ :		
15. How many new patent applications ('priority filings') have been made? <i>("Technologically unique": multiple applications for the same invention in different jurisdictions should be counted as just one application of grant).</i>		1
16. Indicate how many of the following Intellectual Property Rights were applied for (give number in each box).	Trademark	0
	Registered design	0
	Other	0
17. How many spin-off companies were created / are planned as a direct result of the project?		0
<i>Indicate the approximate number of additional jobs in these companies:</i>		
18. Please indicate whether your project has a potential impact on employment, in comparison with the situation before your project:		
☒ Increase in employment, or ☐ Safeguard employment, or ☐ Decrease in employment, ☐ Difficult to estimate / not possible to quantify	☐ In small & medium-sized enterprises ☐ In large companies ☐ None of the above / not relevant to the project	
19. For your project partnership please estimate the employment effect resulting directly from your participation in Full Time Equivalent (FTE = one person working fulltime for a year) jobs:		<i>Indicate figure:</i>

²⁸ Open Access is defined as free of charge access for anyone via Internet.

²⁹ For instance: classification for security project.

Difficult to estimate / not possible to quantify		x
I Media and Communication to the general public		
20. As part of the project, were any of the beneficiaries professionals in communication or media relations? ☐ Yes ☒ No		
21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public? ☐ Yes ☒ No		
22 Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?		
☒ Press Release ☐ Media briefing ☐ TV coverage / report ☐ Radio coverage / report ☒ Brochures /posters / flyers ☐ DVD /Film /Multimedia	☐ Coverage in specialist press ☐ Coverage in general (non-specialist) press ☐ Coverage in national press ☐ Coverage in international press ☒ Website for the general public / internet ☒ Event targeting general public (festival, conference, exhibition, science café)	
23 In which languages are the information products for the general public produced?		
☐ Language of the coordinator ☐ Other language(s)	☒ English	

Question F-10: Classification of Scientific Disciplines according to the Frascati Manual 2002 (Proposed Standard Practice for Surveys on Research and Experimental Development, OECD 2002):

FIELDS OF SCIENCE AND TECHNOLOGY

1. NATURAL SCIENCES

- 1.1 Mathematics and computer sciences [mathematics and other allied fields: computer sciences and other allied subjects (software development only; hardware development should be classified in the engineering fields)]
- 1.2 Physical sciences (astronomy and space sciences, physics and other allied subjects)
- 1.3 Chemical sciences (chemistry, other allied subjects)
- 1.4 Earth and related environmental sciences (geology, geophysics, mineralogy, physical geography and other geosciences, meteorology and other atmospheric sciences including climatic research, oceanography, vulcanology, palaeoecology, other allied sciences)
- 1.5 Biological sciences (biology, botany, bacteriology, microbiology, zoology, entomology, genetics, biochemistry, biophysics, other allied sciences, excluding clinical and veterinary sciences)

2. ENGINEERING AND TECHNOLOGY

- 2.1 Civil engineering (architecture engineering, building science and engineering, construction engineering, municipal and structural engineering and other allied subjects)
- 2.2 Electrical engineering, electronics [electrical engineering, electronics, communication engineering and systems, computer engineering (hardware only) and other allied subjects]
- 2.3. Other engineering sciences (such as chemical, aeronautical and space, mechanical, metallurgical and materials engineering, and their specialised subdivisions; forest products; applied sciences such as

geodesy, industrial chemistry, etc.; the science and technology of food production; specialised technologies of interdisciplinary fields, e.g. systems analysis, metallurgy, mining, textile technology and other applied subjects)

3. MEDICAL SCIENCES

- 3.1 Basic medicine (anatomy, cytology, physiology, genetics, pharmacy, pharmacology, toxicology, immunology and immunohaematology, clinical chemistry, clinical microbiology, pathology)
- 3.2 Clinical medicine (anaesthesiology, paediatrics, obstetrics and gynaecology, internal medicine, surgery, dentistry, neurology, psychiatry, radiology, therapeutics, otorhinolaryngology, ophthalmology)
- 3.3 Health sciences (public health services, social medicine, hygiene, nursing, epidemiology)

4. AGRICULTURAL SCIENCES

- 4.1 Agriculture, forestry, fisheries and allied sciences (agronomy, animal husbandry, fisheries, forestry, horticulture, other allied subjects)
- 4.2 Veterinary medicine

5. SOCIAL SCIENCES

- 5.1 Psychology
- 5.2 Economics
- 5.3 Educational sciences (education and training and other allied subjects)
- 5.4 Other social sciences [anthropology (social and cultural) and ethnology, demography, geography (human, economic and social), town and country planning, management, law, linguistics, political sciences, sociology, organisation and methods, miscellaneous social sciences and interdisciplinary, methodological and historical S1T activities relating to subjects in this group. Physical anthropology, physical geography and psychophysiology should normally be classified with the natural sciences].

6. HUMANITIES

- 6.1 History (history, prehistory and history, together with auxiliary historical disciplines such as archaeology, numismatics, palaeography, genealogy, etc.)
- 6.2 Languages and literature (ancient and modern)
- 6.3 Other humanities [philosophy (including the history of science and technology) arts, history of art, art criticism, painting, sculpture, musicology, dramatic art excluding artistic "research" of any kind, religion, theology, other fields and subjects pertaining to the humanities, methodological, historical and other S1T activities relating to the subjects in this group]

1. FINAL REPORT ON THE DISTRIBUTION OF THE EUROPEAN UNION FINANCIAL CONTRIBUTION

This report shall be submitted to the Commission within 30 days after receipt of the final payment of the European Union financial contribution.

Report on the distribution of the European Union financial contribution between beneficiaries

Name of beneficiary	Final amount of EU contribution per beneficiary in Euros
1.	
2.	
n	
Total	