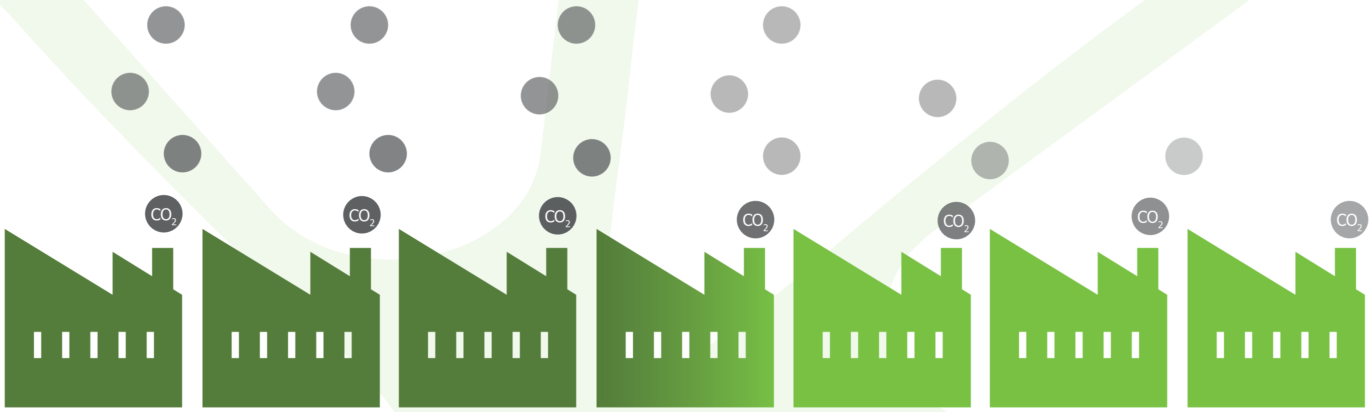
NanoMaterials Enhanced Membranes for Carbon Capture



Enjoy reading the NANOMEMC² newsletter!

The NANOMEMC² project started in October 2016 and is a research and innovation action of Horizon 2020 funded under the topic LCE-24-2016 "International cooperation with South Korea on new generation high-efficiency capture processes".

It aims at reducing the cost, energy and process limitations which currently make pre and post-combustion CO_2 capture processes non-viable in many industrial applications. Through the development of innovative materials, membranes and membrane processes for CO_2 capture, the project aims to make possible a substantial reduction in energy penalty, a much lower cost and a reduction of CO_2 emissions.

This will allow for a radical step change in the deployment of Carbon Capture and Storage (CCS) technologies across EU industry, unleashing its potential for significant CO_2 emissions savings, which are key to reaching European targets for a more sustainable industry. In doing so, the project will seek strong collaboration with Korean counterparts on the basis of a common research path and strategy.

NANOMEMC² is in the first semester of its second year. Continue reading this newsletter to find out more about the main activities and results achieved so far and plans for upcoming period.

CONTENTS

WP1 - coordination and management

The core work of WP1 is related to the coordination and monitoring of project activities, the administrative and financial management, the coordination of the reporting and deliverables production, as well as the management of the knowledge generated and the resolution of possible conflicts, aiming to facilitate other WPs activities. Current project management activities are in line with the initial expectation and no substantial problems have been encountered in both project and consortium management. Communication with the European commission remained fluid and efficient. Project meetings are held regularly and successfully in terms of both organization and participation. Next project meeting will be organized in March 2018 in Sheffield (UK) and will be coupled with a scientific dissemination workshop. AB members will be also invited to this midterm project meeting.

Fig.1 – NANOMEMC² partners at the kick off meeting in Bologna, Italy, 10-11 October 2016 (month 1 of the project)

WP2 - Material development and characterization

AIMs and CURRENT ACHIEVEMENTS

The aim of the WP is to fabricate and optimize hybrid polymer-based **membranes** for CO_2 capture. **In the first year of the project, a total of 55 different membrane materials were produced and characterized**; 29 for application as Facilitated Transport Hybrid Membranes (FTHMs) and 24 for Continuous Phase Hybrid Membranes (CHPM) production. The most promising were sent to WP3 for the analysis of permeation and separation performance.

NANOFILLERS

Few layer graphene, obtained by exfoliation of graphite, is used in the project. The gas transport can occur between layers. Graphene is insoluble but can be dispersed in several polymers. It can be modified to produce Graphene Oxide (GO) which is characterized by a non-perfect 2d structure, presence of voids and defects that are permeable and selective. It can be dispersed in water and thanks to the defects and functional groups present in the structure it can be chemically modified to add specific functionalities.

Nano Fibrillated Cellulose (NFC) is produced by mechanical disintegration of cellulose wood fibers, it can be obtained in the form of water suspension (gel), powder or self-standing films. It is highly hydrophilic, has high mechanical strength and excellent oxygen barrier properties in dry state. It helps reducing the swelling of membrane during FT processes. In general, it acts a natural reinforcement and can be chemically modified to increase hydrophobic character or add new functionalities.

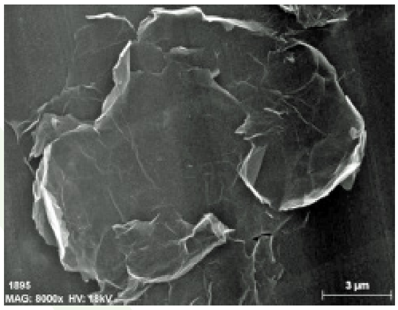


Fig. 2 - Few layer Graphene

MEMBRANES

FTHMs: CO_2-selective Hybrid membranes for post-combustion facilitated transport (FT) processes bearing amine groups to boost CO_2 capture, incorporating water-stabilizing agents like nanocellulose (NFC) and graphene. FT is a reaction-enhanced permeation process and allows FTHM to surpass the Robeson's Upper bound which limits the solution-diffusion membranes. In the picture, a Polyvinylamine-GO membrane is shown produced by UNIBO in the 1st year.

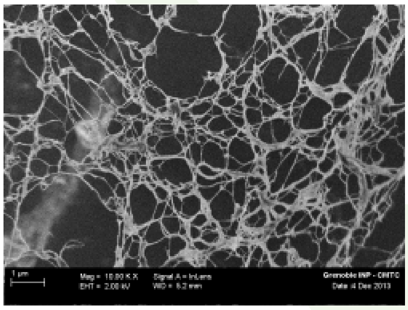


Fig. 3 - Nanofibrillated Cellulose (NFC)

CPHMs: They are based on size-sieving polymeric matrices and a nanofiller for pre-combustion processe (H_2/CO_2 separation). Intrinsic permeability and selectivity of nanofillers, and their ability to modify at the nanoscale the distribution of polymeric chains makes, is exploited to optimize the CO_2 capture performance. Previous studies encourage the use of Graphenic compounds in gas separations. In the picture a SEM image of a Polymer-GO thin membrane coated over a support is shown, produced by NTNU in the 1st year.

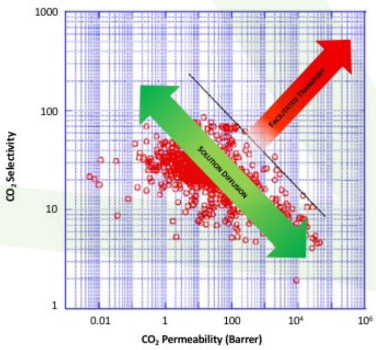


Fig.4 - Performance of FTHM in the Robeson Plot

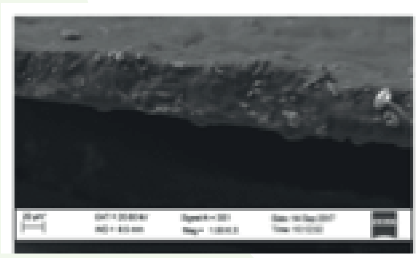


Fig. 5 - One Composite FTHM based on polyvinylamine and GO (UNIBO)

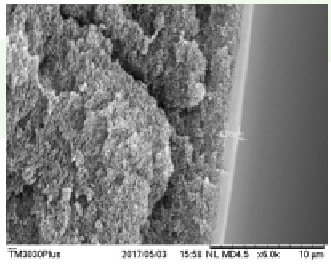


Fig. 6 - Thin film composite CPHM based on PEG and GO (NTNU)

Do you want to read more about the NANOMEMC² membranes? Project partners UNIBO and Graphene XT just published a paper on the "Permeability and Selectivity of PPO/Graphene Composites as Mixed Matrix Membranes for CO_2 Capture and Gas Separation" in the scientific journal Polymers, download it here.

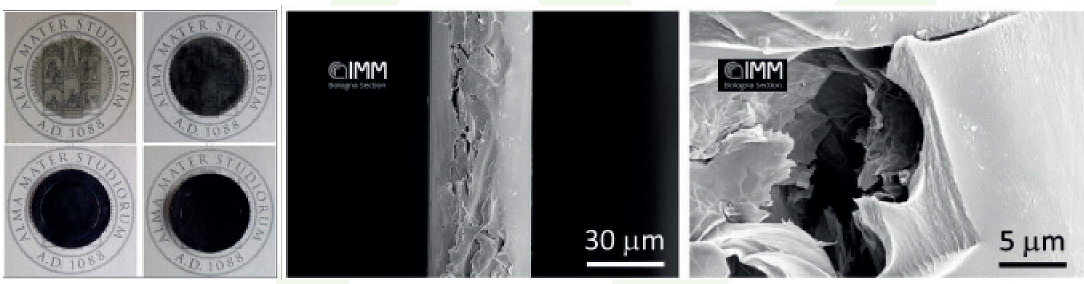


Fig. 7 - Left: Pictures of the various membranes fabricated; right: SEM images of various membranes.

WP3 - CO_2 capture performances

The various membranes fabricated in WP2 have been tested using different gases in order to characterize their performance for the gas separations of interests. Depending on the type of material (hydrophobic or hydrophilic) and the type of membrane prepared (self-standing or thin composite), permeation tests using pure or mixed gases, as well as dry or humid gaseous stream have been carried out. Mild test conditions in terms of temperature (25 – 65 °C) and pressure (1 – 2 bar) have been used to screen among the fabricated membranes. In the following description, permeability is reported in Barrer (1 Barrer = 3.346 x 10^{-16} mol m^{-1} Pa^{-1} s^{-1}), whereas permeance is in GPU (1 GPU = 3.346 x 10^{-10} mol m^{-2} Pa^{-1} s^{-1}).

Polyphenylenoxide (PPO) membranes containing different types of graphene (graphene oxide, GO, and graphene) in different amount were characterized in terms of CO_2, N_2 and He permeability (Fig. 8). For small amount of graphene (1 wt%) and GO (0.3 wt%) an increase in gas permeability is observed (up to 20% of the pure PPO value). However, for higher loadings a permeability drop is observed, may be due to the impermeable nature of graphene. Negligible effect on gas selectivity is observed. When the operating temperature is increased to 65 °C, similar results have been obtained.

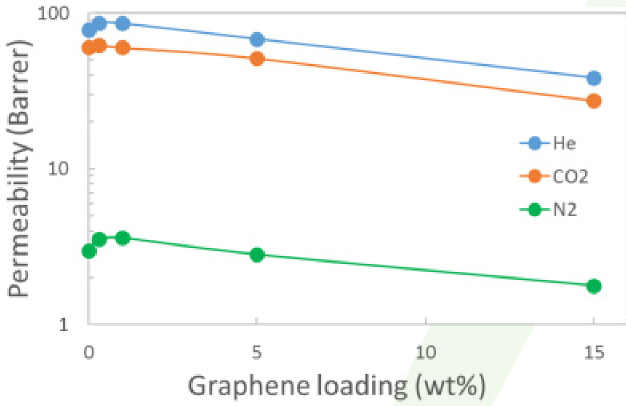


Fig. 8 - Performance of PPO+Graphene membranes, 35 °C, 1 bar

Graphene and GO have also been added to polyvinylamine (PVAm), which is a hydrophilic polymer that can lead to facilitated transport of CO_2 through the selective layer, thanks to the presence of amine group. Upon the purification of the commercial product (Lupamin) following different methods (PVAm M3 and PVAm M5), the GO was added to the matrix and the membranes have been tested under different level of humidity. Indeed, fully dry PVAm is almost impermeable due to the high crystallinity, and water vapor is needed to swell the matrix and allow the permeation of gaseous penetrants. The addition of graphene-based nanoparticles determines a small drop in the CO_2 permeability, but it is believed to be able to improve the mechanical stability of the membrane. Interestingly, **better results** (both in terms of permeability and selectivity) **can be achieved by adding nanocellulose fibers (NFC) to the PVAm matrix**. In this case, the nature of the nanoparticles allows the NFC concentration increasing in the polymeric solution to up to 50 wt%. The high selectivity of the NFC phase leads to the achievement of a promising performance: at a relative humidity higher than 90%, the membrane performance are able to cross the upper bound of the state-of-art (black line in Fig. 9) for the particular gas pair.

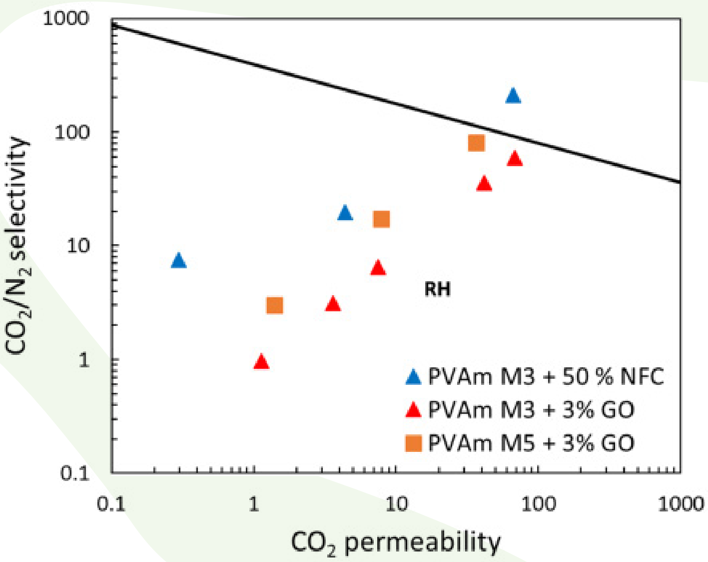


Fig. 9 – CO_2/N_2 separation performance of PVAm-based membranes containing graphene and nanocellulose phases. Relative humidity (RH) increased from 50% to 92% in both feed and sweep streams.

Interesting separation performance were also obtained for the membrane prepared by blending ionic liquids (ILs) and NFC. As reported in Fig. 10, the addition of ILs into the NFC matrix helped in considerably increasing the CO_2 permeability in the entire RH range, reducing the influence of humidity on the membrane performance. Different type of ILs [Emim][OAc], [Emim][Cl], [Bmim][DCA], [Bmim][NO_3] have been used to prepare hybrid membranes due to their good compatibility with NFC and high CO_2-philicity. Among the tested ILs, [Emim][OAc] showed the best performance in the mixed gas permeation test: under fully saturated conditions and using a stream with a 10 vol% CO_2 in N_2, the sample containing 50% IL has shown a CO_2 permeability close to 300 Barrer and a CO_2/N_2 selectivity of about 60, remaining above the upper bound. Similar trends have been observed also for CO2/CH4 performance, but lower selectivity have been obtained due to the higher solubility of CH4 in the membrane compared to N_2.

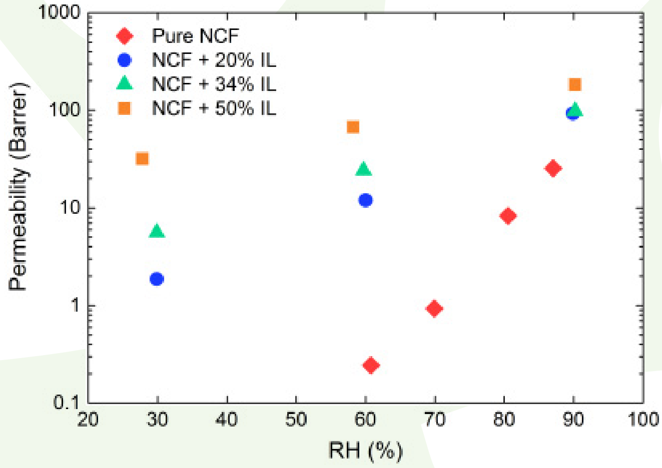


Fig. 10 – Influence of [Emim][OAc] content on the CO_2 permeability of NFC membrane (single gas permeation test)

Since the final scope of the project is to maximize the membrane performance, thin composite membranes have been prepared using polyvinyilalcohol (PVA) and polyallylamine (PAA). Subsequently, the membrane composition has been changed by adding different types of nanocellulose. Selective layers with a thickness in the order of 300 – 700 nm have been coated on commercial polysulfone (PSF) flat sheets and PPO hollow fiber membranes. Due to the achievement of such thin layers, efforts have also been put in the determination of the influence of the porous support. In particular, the PSF initially used was found to be a possible bottleneck to the achievement of high CO_2 permeance. Better results were achieved with the PPO hollow fibers. Interestingly, it has been found that **when cellulose nanocrystals (CNC)** instead of CNF **have been dispersed in a PVA matrix, a larger increment of the CO_2 permeance (+ 50%) can be achieved** with a limited effect on the membrane thickness. CO_2 permeances close to 700 GPU have been obtained. The addition of nanocellulose, however, has led to a negligible effect on selectivity (remaining around 40 in the case of CO_2/N_2).

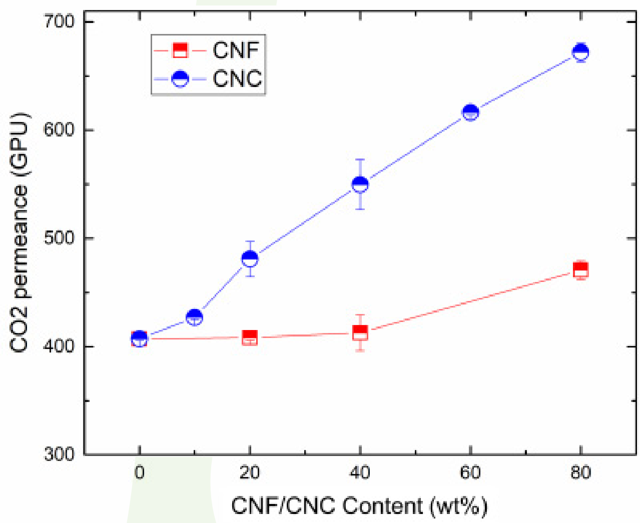


Fig. 11 – CO_2 permeance of PVA-based membranes containing different amount of CNF and CNC. Tested under fully humidified conditions.

WP4 - Materials and membranes modelling

WP4 focuses on the material modelling in order to retrieve key information on the relationships between structural and transport properties. This information will be used for both material design and prediction/description of membrane performances alone and in the framework of process simulation.

Two-level approach is employed. At the macroscopic-level, we are building structure-property relationships by exploring the available experimental data and training the models to predict properties of the membranes. At the molecular level, molecular simulation approaches are used to construct realistic models of polymer membranes; understand their structural characteristics; provide molecular level models of solubility and diffusivity of relevant species within these structures. Ultimately, the main objective of molecular modelling is to provide an explanation and a molecular picture of the facilitated transport phenomena.

First year results include the testing and parametrization of existing macroscopic models to available permeability data. After an extensive bibliographic search, a mathematical model was tested, based on a simplified diffusion+reaction scheme, that was tested and validated on 3 different fixed carrier FTHM from literature (see Figure 12). Parameter values are reasonably close to experimental values, with the exception of diffusion coefficients.

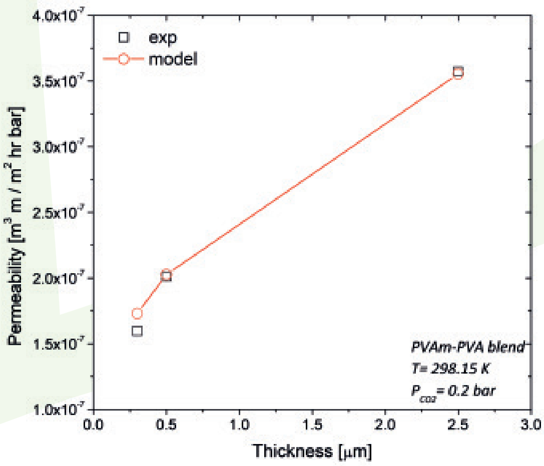


Fig. 12 - Permeability vs. Membrane Thickness for PVAm/PVA blend membrane. CO_2 Feed Pressure = 0.2 bar.

The 2nd year of project activity is devoted to the development of new predictive tools for evaluating a priori the basic parameters like diffusivity, solubility and finally estimate the permeability of FTHM. Binary systems are first modelled, with the final aim of modeling the ternary system polymer-water-carbon.
The PC-SAFT equation of state (Gross, Sadowski, 2001), was used to model the water vapour sorption in polyvinylamine (PVAm) and CO_2 sorption in liquid H_2O. Acid-base interactions were modeled with different association schemes, finding the best one (Figure 13).

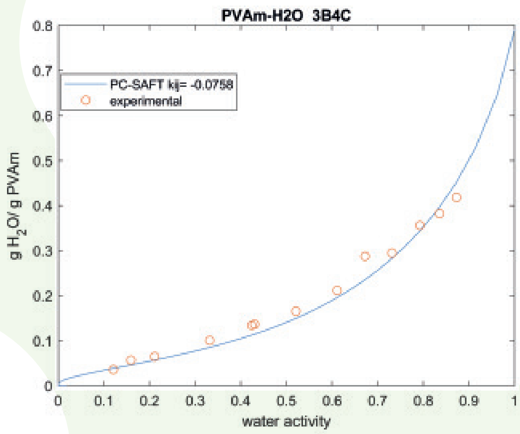
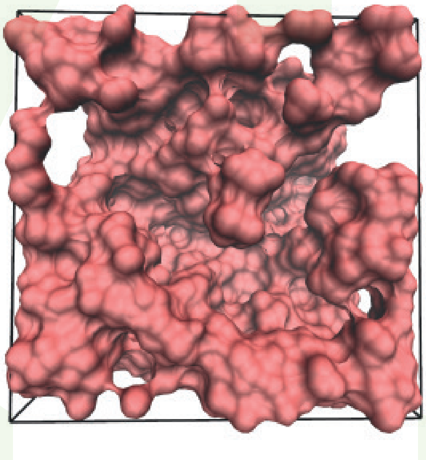


Fig. 13 - PVAm-H_2O PC-SAFT modelling results for 3B4C association scheme

Water diffusion in PVAm was modeled with the hydrodynamic scaling model given by Phillies while the Stokes-Einstein equation was used for CO_2 diffusion in liquid water.
On the molecular level, the research evolved along two directions. Development of accurate models of solubility of various gases in model polymer membranes is challenging as the data required for model validation is scarcely available. Our strategy considers a preliminary stage focusing on molecular models of solubility of gases in amine solutions, as these systems reflect chemistry similar to that of polyamines solution, but at the same time there is extensive experimental data available for validation. Hence, accurate models of solubility of methane, nitrogen and (non-reacting) carbon dioxide in water-MDEA solutions have been developed and validated. In the co-current research track we explored different approaches to the construction of model water-swollen polymer structures. This involved quantum

mechanical studies of charge distribution along PVAm chains, molecular level interactions between carbon dioxide and PVAm molecules and between water and PVAm molecules. Several models of water-swollen PVAm (under conditions where PVAm is not protonated) have been constructed and their structural characteristics as well as dynamics of confined water explored as a function of the water content.



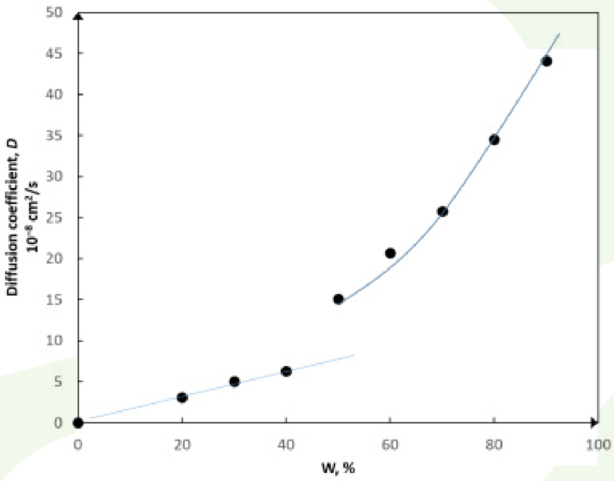


Fig. 14 - Molecular model of water swollen PVAm membrane (on the left, water is not shown) and water diffusion coefficients as a function of water loading (on the right).

The **next steps** are associated with reconciling the results for macroscopic and molecular models (solubility, diffusivity) in the regimes where they should agree with each other; developing molecular models of PVAm membranes reflecting different degrees of protonation; exploring molecular diffusivity of the ionic species in realistic models of PVAm membranes as a function of water content, pH, presence of other species and so on.

WP5 - Process Design, Optimization and Assessment

The activities on "Process Design, Optimization and Assessment" focus on implementation of the novel NANOMEMC² carbon capture technologies into the whole production processes and the evaluation of their economic and environmental performances under industrial conditions (Work package 5). Hence, the new technologies are applied to Industrial Production Scenarios which allows demonstrating their benefits by comparison towards existing "Business As Usual (BAU)"-cases, making use of standard technologies and conventional production routes applying no means of carbon capture, and modifications thereof using state-of-the-art CCS-technologies.

For a significant comparability of process alternatives, extensive system-integration of the production processes and their capture technologies is required. Naturally, this involves the consideration of constraints related to a particular industrial process to a full extent, but facilitates tapping potentials for synergies with up- and downstream operations.

To identify most promising Industrial Production Scenarios for the application of the innovative technologies and materials developed, a broad range of industrial key sectors such as power generation, oil & gas processing, cement production, iron & steel, chemical industry, glass & mineral production etc. was screened. From the multitude of the resulting process alternatives, those considered industrially relevant and noted for contributing to climate change by the emission of carbon dioxide were selected for further analysis. These processes were characterized in a scouting manner; by the application of the systematic, multi-criterial NANOMEMC²-selection-procedure the number of Industrial Production Scenarios was narrowed down to the following technologies for a detailed investigation:

- Natural gas based power production

- Cement production processes
- Hydrogen production via steam methane reforming
- Integrated coal gasification combined cycle power plants

In close collaboration with the industrial end users of technology such as BP International Ltd. and COLACEM SPA as well as with the academia University of Sheffield, the partners SUPREN GmbH and the University of Edinburgh conduct the process development and the costing of the identified process alternatives. To complete the overall picture, the project partner CIAOTECH Srl. assesses the environmental performances of production scenarios in parallel: through a Life Cycle Assessment study in accordance with ISO 14040:2006 and 14044:2006, the Global Warming Potential (GWP) of the identified industrial processes is analyzed with a cradle-to-grave approach, i.e., by considering the entire production chain from raw materials to production and usage phases to products final disposal.

For the time being, mass & energy balances have been established for each aforementioned production scenario. Besides the conventional BAU-cases, concepts using various state-of-the-art pre- and post-combustion carbon capture technologies such as selective absorption/desorption processes exploiting diverse solvents or the exploitation of existing gas-separation-membranes have been analyzed.
For all investigations care is taken to progress in alignment with the information provided by relevant institutions such as EBTF, CEMCAP and IEAGHG to ensure a far-reaching significance of the results obtained.

WP6 - Module development and prototype testing

WP6 is devoted to scale up of the most promising membranes developed in WP2 and to test them under operating conditions identified in WP5 as the most suitable for high efficiency industrial capture. The work will focus on the scale up of the flat sheet / hollow fibre membranes, the development on the membrane modules and the design and construction of the test rigs to be able to test the membranes in the desired conditions.

Most of the activities will start in the 2nd year of the project. During the first year partners made first estimations about:

- Membrane limitations
- Module limitations
- Available feed gas composition

Next steps will be the actual start of upscaling the membranes and development of the modules and test rigs for the actual tests.

WP7 - Dissemination of results

Dissemination and communication activities are a key aspect of the project NANOMEMC^2 and include the delivery of the project concept, vision and results to the largest possible audience to engage every stakeholder at European and global scale.

To this aim, the NANOMEMC^2 website has been set up and a detailed Dissemination and Communication plan agreed among partners. The project's results and updates are constantly presented online (websites, social medias…) and offline (publications in relevant scientific journals, presentations in international meetings and conferences, newsletters...). Key events attended by partners include:

- **9th Trondheim conference on CO_2 capture, transport and storage**, 12-14th June 2017, Trondheim, Norway
- **ICOM 2017**, International conference on membrane and membrane processes, 29 Jul - 4 Aug 2017, San Francisco, US
- **H2020 CCS/CCU and alternative fuels projects clustering event**, 15 May 2017, Bruxelles, Belgium
- **8th Korea CCUS International Conference**, 24-26 January 2018, Jeju, KR

The first dissemination workshop of the project with predominantly scientific/academia focus will be held at the **University of Sheffield, UK, on the 20th of March 2018.** Interested in joining the workshop? You can find the agenda and registration info on the project NANOMEMC² website.
Project newsletters are published each six months to update stakeholders about the most recent results. The collaboration with two projects, ROLINCAP and GRAMOFON, funded by EC in the same NANOMEMC² framework of Topic LCE-24-2016, resulted in two joint newsletters (one already published, second one in preparation).

WP7 - Exploitation of results

The NANOMEMC² project will produce several results with high scientific and industrial impact over the next two years which could be considered for further exploitation. On the industrial side, several products will be developed and validated in industrial environment during the project, becoming thus potentially suitable for exploitation.
Several activities have been performed during the 1st year of the project towards the implementation of an effective exploitation:

- **A stakeholder analysis**, as a basis for the project's exploitation strategy, was carried out by NANOMEMC² partner PNO in collaboration with all project partners. The analysis aimed to identify the most important stakeholders of the NANOMEMC² solution(s) (research centres, companies and industrial associations) and assess their position towards the project's results to setup engagement strategies for dissemination and exploitation activities and to establish links and develop synergies with on-going EU projects for mutual benefit;
- Partners involved **selected key stakeholders** in the innovation process by inviting them to participate in **one-to-one interviews** (led by PNO), in order to:
  - i) measure stakeholder characteristics, e.g. their interest, attitude, influence and knowledge relevant for the project;
  - ii) receive expert feedback on market(s) data, competition, trends and dynamics and elements to investigate preliminary market interest.

  Selected stakeholders include associations focused on carbon capture and storage, research organizations working on membrane and companies from several sectors (material suppliers, oil and gas producers; chemical companies) and from all Europe.
- A preliminary **description of the approach to exploitation, expected results and required activities for creating impact** was created through consultation with all partners of the consortium;
- **The first exploitation workshop was organized** on the 26th of October 2017 in Rome, taking advantages from the Support Services for Exploitation of Research Results (SSERR) offered by the European commission (EC). The consultant Dr. A. Di Anselmo designed by the EC explained the EC rules of exploitations, expectations, requirements, etc. Project partners PNO and FUJIFILM guided the following discussion among partners on the definition of the preliminary list of the Key Exploitable Results (KERs).

In the next two years, using the results from the life cycle assessment (LCA) and the techno-economic assessment carried out in WP5, a NANOMEMC[2] business plan will be created, with the aim of exploring the marketability of the proposed solution(s) and to lay down the main strategies for future deployment and commercialisation. The **business plan** will include the identification of the real market(s) for the CO_2 capture technology, accompanied by a market survey as well as an evaluation of the market size and competing technologies on the identified market(s).

WP8 - Twinning activities with Hanyang University, South Korean partner of NANOMEMC² project

Work Package 8 is dedicated to the organization and managements of all the twinning activities and interactions among the NANOMEMC[2] consortium partners and Hanyang University, where Professor Ho Bum Park is currently leading the project "Engineering technology developed for high transmission channel pore selective CO_2 membrane material". The collaboration between the two projects is based on the exchange of Information, Materials, Data and Researchers.

Exchange of Information

The exchange of information aims at helping the different groups involved in the Twinning activities to initially know each other, to find complementary expertise and to discuss directly project outcomes and possible common developments.

Activities started in month 2 with the first meeting between the project coordinator, Prof. Baschetti, and Prof. Park at the AIChE 2016 Annual meeting in San Francisco. Activities carried on through the organization of teleconferences and web meetings to start exchanging information and input on current status of their researches. The first webinar took place on the 11th of May 2017 and focused on a presentation of the activities currently performed in the field of carbon capture with membranes in Prof. Ho Bum Park's Group. Following this, different webinars have been scheduled in order to share information about progress activities within the consortium; a second webinar was delivered by WP2 on the 11th of September 2017 and focussed on the materials already developed in the project.

In month 8 (June 2017), the first Joint project meeting was organized in Trondheim following the first Joint workshop between INEA funded projects.

A second twinning workshop has been organized by the Korea Carbon Capture & Sequestration R&D Center during the 8th Korea CCUS International Conference which took place in Jeju Island (KR) from 24 to 26 of January 2018.

Fig. 15 - Social dinner in Trondheim. Prof. Baschetti, Prof. De Angelis, Dr. Ferrari, Prof. Park and Prof. Deng enjoying good food and an amazing landscape while strengthening their collaboration.

Exchange of Materials

Materials (different type of nanofillers) and membranes will be exchanged by the different partners of the two projects. This activity will be carried out according to a specific Non Disclosure Agreement (NDA) approved by both the European and Korean side.

Exchange of Data

Experimental results concerning membrane properties and performance will be exchanged between partners to build a common database of the project outcomes.

A specific shared database will be constructed to which both EU and Korean partner will have free access. The database will be hosted on the project website and monitored by WP8 but will be compiled by all the partners and WPs as they carry out their activities.

Fig. 16 - Dr. Ferrari presenting NANOMEMC2 results at the second twinning workshop in Jeju Island (KR).

Exchange of Researchers

Short term scientific missions (STSM) are organised to perform specific activities in the twin project facilities, to work on the exchanged materials characterisation and modelling as well as on different topics agreed between the partners.

The exchange of researchers started in Month 13 with the visit of a young researcher from the NANOMEMC^2 project to Korea. This exchange was focused on the materials synthesis following the Korean partners expertise (graphene based coatings and membranes). A PhD student from NTNU (Saravanan Janakiram) visited Prof. Park's group from the 27th of October for two months.

A second researcher from NTNU (Zhongde Dai) is currently (expected end of STSM February 3rd) in Korea focussing on the development of thin films.

Fig. 17 - Saravanan Janakiram from NTNU visiting Prof. Park group and Zhongde Dai in Prof. Park's lab in South Korea.

The first exchange from Korea to EU will take place in Month 16 and will involve a young researcher and the development of the second generation of materials.

How can you engage with the NANOMEMC² project?

If you want to learn more about the NANOMEMC² project, visit the website at www.nanomemc2.eu and subscribe to the newsletter, or Follow the project on the social.

Follow our NanoMEMC² tweets on Innovation Place and CiaoTech

Follow our NanoMEMC² news on Innovation Place

Follow us on Facebook

Follow us on Research Gate

To get in touch with one of the NANOMEMC² partners, please e-mail a.dellapia@ciaotech.com or visit the website contact page.

NANOMEMC² consortium

The NANOMEMC² consortium involves 11 partners and covers the whole value chain of the newly developed carbon capture solutions. More information about the involved organisations and their role in the project can be found in the first NANOMEMC² newsletter, which can be found here.

ALMA MATER STUDIORUM
PROJECT COORDINATOR
www.unibo.it

NORGES TEKNISK-NATURVITENSKAPELIGE UNIVERSITET NTNU
www.ntnu.no

THE UNIVERSITY OF EDINBURGH
www.carboncapture.eng.ed.ac.uk

THE UNIVERSITY OF SHEFFIELD
www.energy2050.ac.uk

BP INTERNATIONAL LIMITED
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COLACEM SPA
www.colacem.com

FUJIFILM MANUFACTURING EUROPE BV
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SUPREN GMBH
www.supren.eu

GRAPHENE-XT
www.graphene-xt.com

INOFIB SAS
www.inofib.com

CIAOTECH SRL
www.pnoconsultants.it

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