



**MemCCSea**

Innovative membrane systems  
for CO<sub>2</sub> capture and storage at sea

# MemCCSea: Carbon Capture at sea

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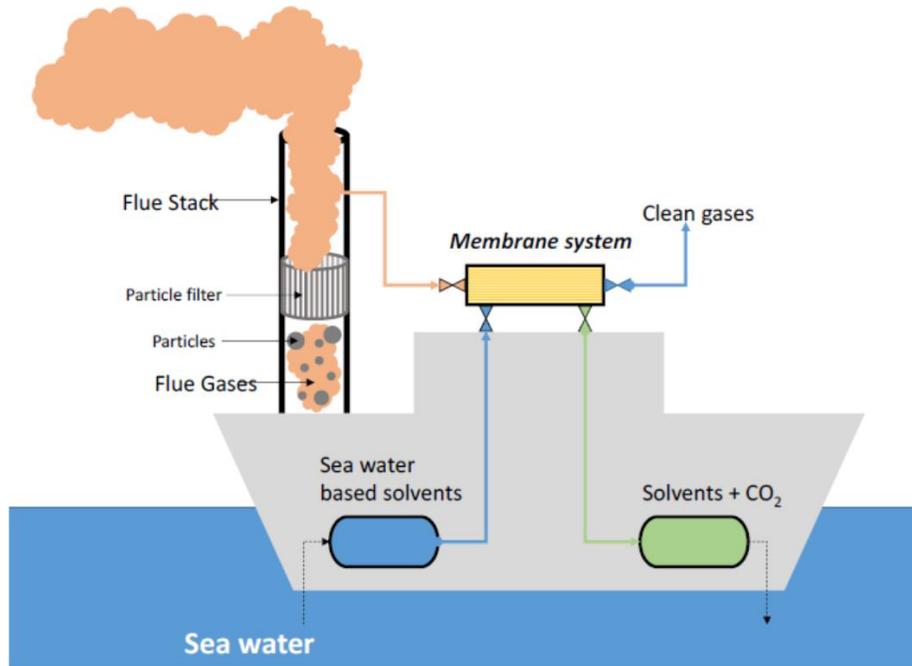
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**Chemical Process & Energy Resources Institute**  
**Centre for Research & Technology Hellas**

# Project Concept & Key Objectives

## The MemCCSea Concept

Development of **hyper compact membrane systems** for flexible operational and cost-effective **post-combustion CO<sub>2</sub> capture** in **maritime and off-shore applications**.



## Key Objectives

Provide a **feasible design** and **pilot demonstration**, optimized for maritime applications, capable to achieve **higher than the state-of-the-art performance**, meeting the following key targets

- Recovery of the **main engine CO<sub>2</sub> emissions greater than 90%**
- **Overall CO<sub>2</sub> emissions reduction** (including added emissions by the capture plant and utilities **greater than 50%**)
- **A 10-fold reduction of system volume** and a **reduction of operating costs greater than 25%** compared to a conventional amine-based scrubbing system.

# Project Impact

**GHG emissions** from international shipping **have risen by more than 30%** over the last 30 years, a larger increase compared to every industrial and transport sectors except international aviation, with **increases up to 250%** compared to current levels expected until 2050.

**Strict regulations for CO<sub>2</sub> emissions** from shipping (40% reduction of GHG emissions by 2030, 11% reduction in carbon intensity by 2026) and are reflected in updated calculation of key efficiency indices (EEDI, EEXI, CII)

## Active participation of industry & classification society



Leading crude oil tanker shipping company worldwide



Leading EU classification society

## Active participation in related CCS projects for energy-intensive industries



Carbon capture and mineralization in the cement industry



CERESIS



Membrane-based CO<sub>2</sub> separation processes in the biofuels production industries

**EPS AND VALUE MARITIME ANNOUNCE AGREEMENT** 2022

Eastern Pacific Shipping and Value Maritime team up to install the first carbon capture solution onboard a pair of tankers

*The Singapore-based tonnage provider will retrofit two MR tankers with carbon capture systems, making them the largest ocean-going vessels fitted with carbon capture technology to date*

17 MAY 2022

**2x MR TANKERS TO BE FITTED WITH CARBON CAPTURE SOLUTION**

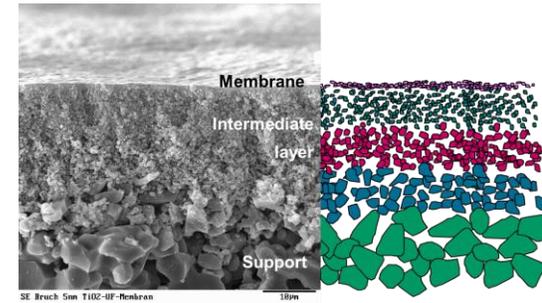
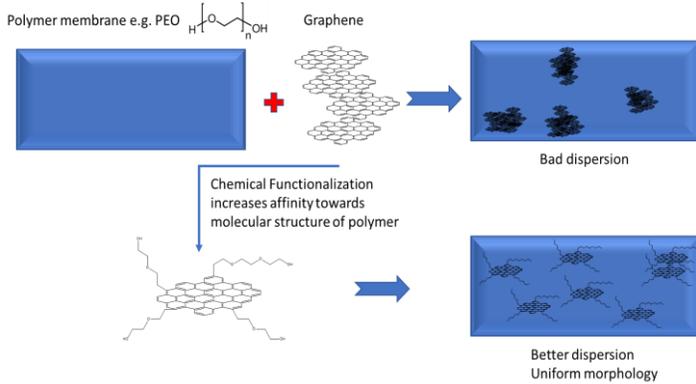
EASTERN PACIFIC SHIPPING | VM | Value Maritime

Japanese shipbuilding giant Mitsubishi announced on Monday (31 August) that it will build and test a carbon-capture system for ships, aimed at significantly reducing the emissions of the maritime sector.

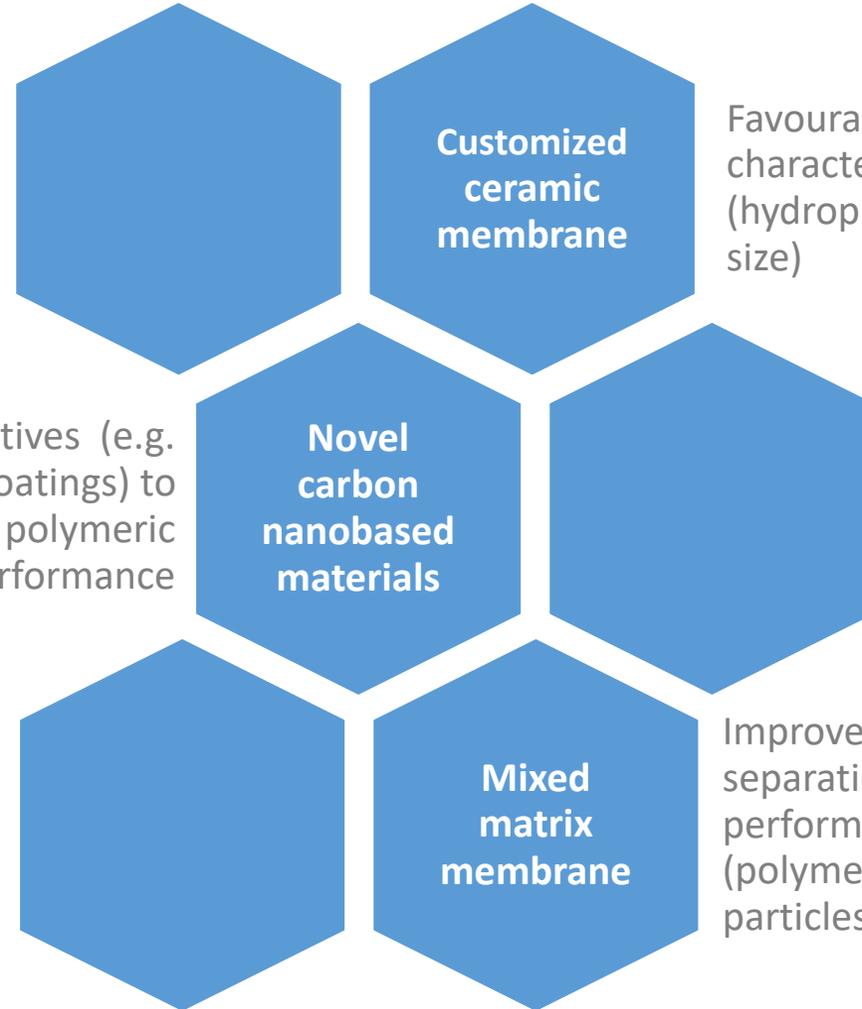


# Project Technology

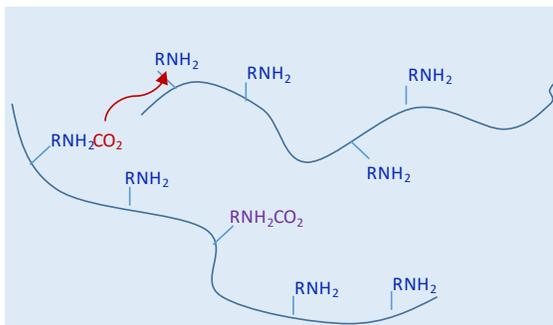
## Re-design and optimization of membranes materials and processes



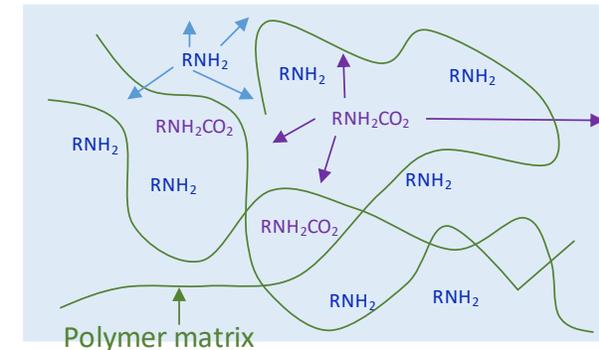
Additives (e.g. Graphene/GO coatings) to enhance polymeric membrane performance



CO<sub>2</sub> "hopping" between fixed carrier sites



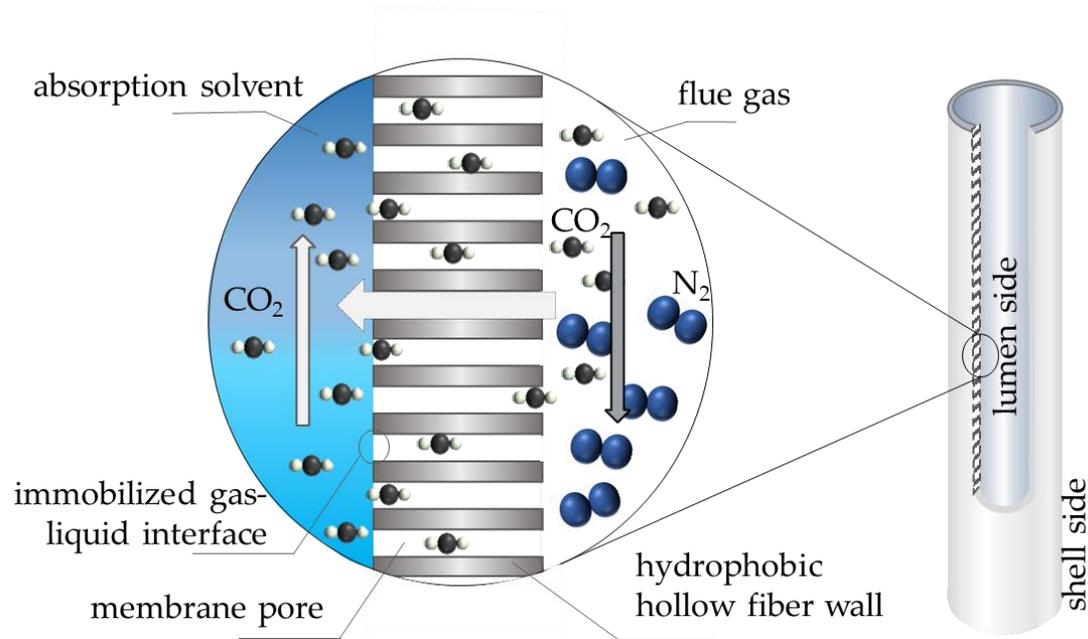
Carrier and Carrier-CO<sub>2</sub> complex are free to diffuse within membrane



# Project Technology

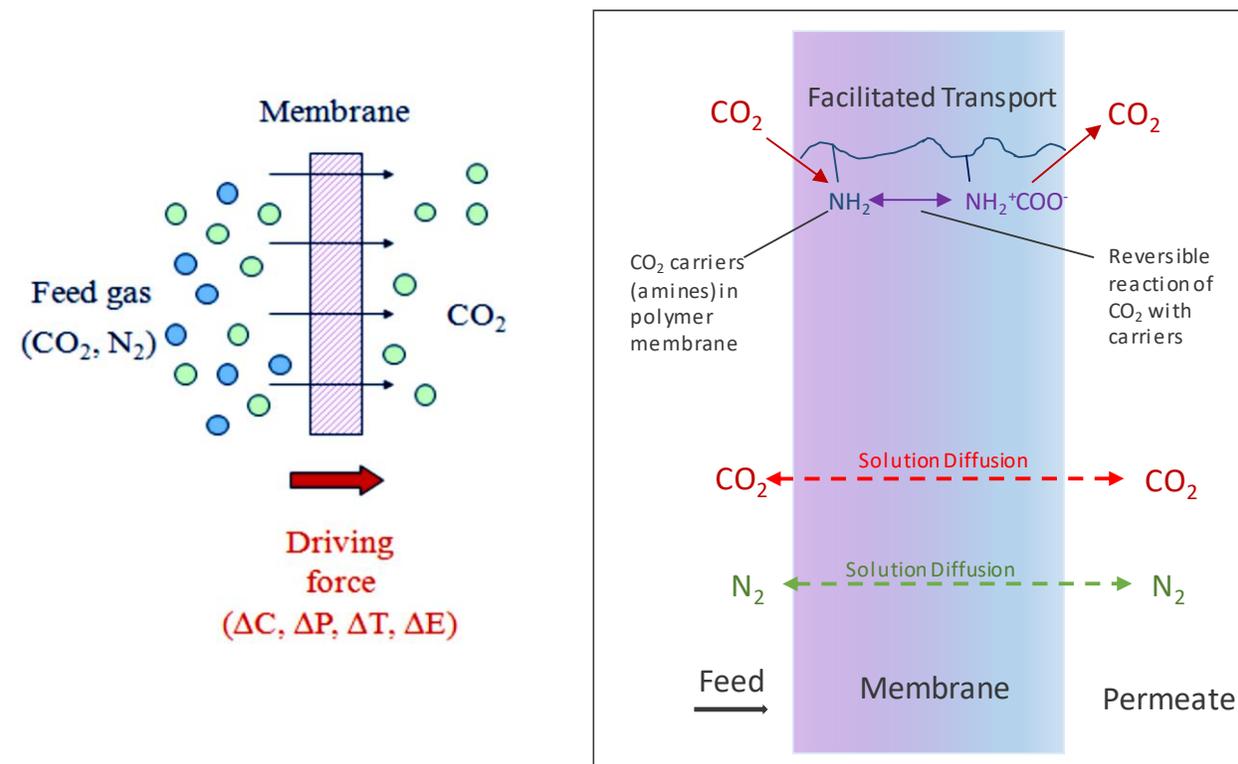
## Re-design and optimization of membranes materials and processes

### Membrane Technology | Gas-Liquid Contactors



Cross section of a porous hollow fiber wall

### Membrane Technology | Permeators



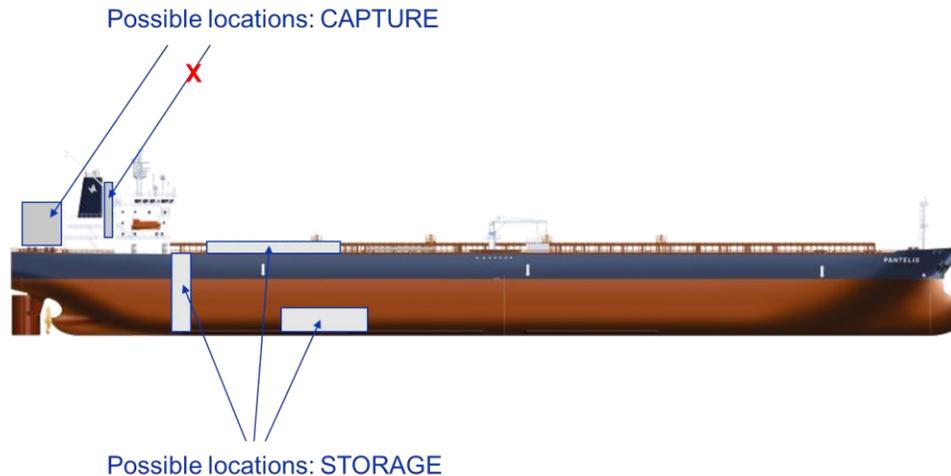
Cross section of a dense membrane wall during CO<sub>2</sub> separation

# Project Innovation

## *Process Marinization*

Design and utilization of environmentally-friendly, **seawater-based solvents** modified with CO<sub>2</sub> capture promoters (e.g. amines, NaOH etc)

Address **unique challenges of maritime environment** (operational and safety requirements, energy efficiency, on-site solvent regeneration etc)



## *Modelling and simulation*

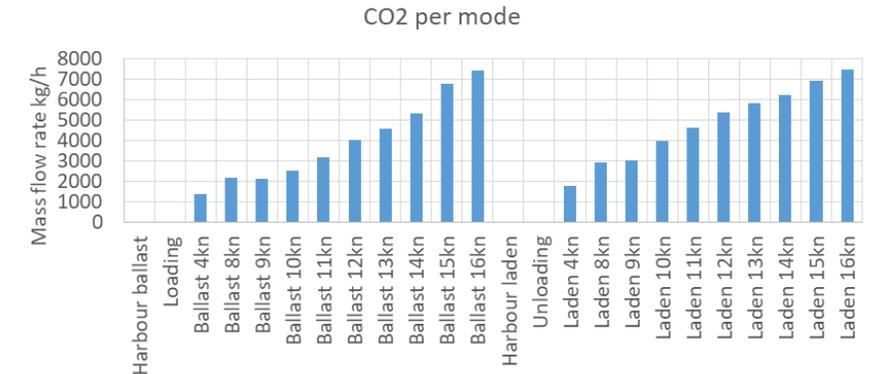
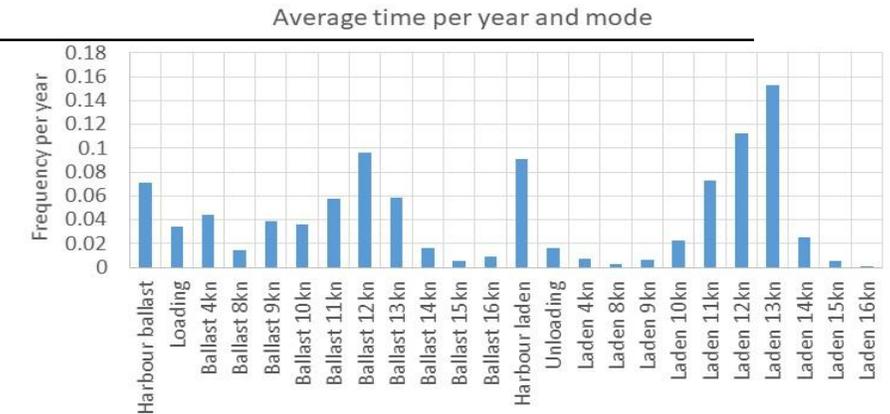
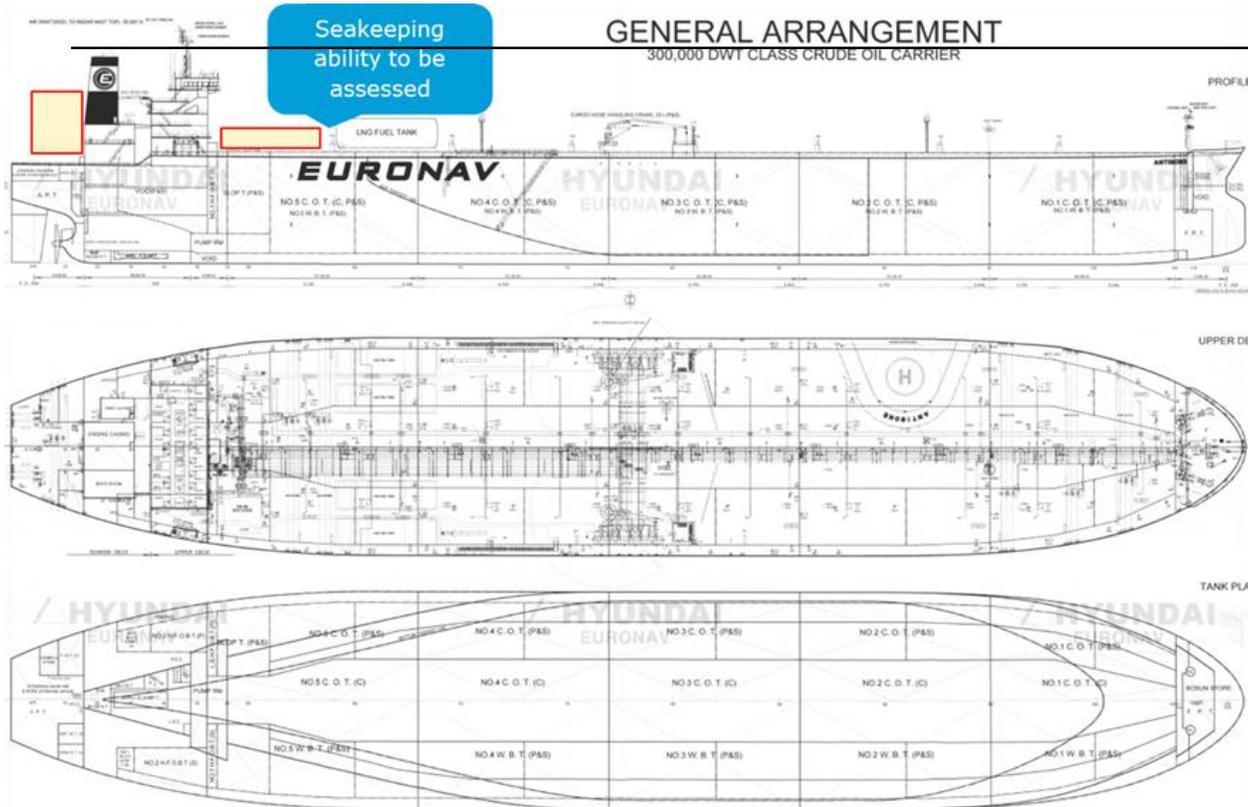
Modelling and simulation of **transport phenomena in CGL and MMP membranes** incorporating accurate material properties and properties of the solvent mixture.

**Model-based assessment and optimization of the marine energy system** with carbon capture (COSSMOS software).

# Definition of process requirements & specifications

## Maritime case specifications (Task Leader: DNV)

### Very Large Crude Carrier (VLCC) with a dual-fuel (MDO/LNG) engine – Trade analysis



# Definition of process requirements & specifications

## Maritime case specifications (Task Leader: DNV)

### Definition of specifications

- Machinery specifications
- Operational conditions
- Key performance metrics
- Storage integration options

### Key Performance Indicators

- CO<sub>2</sub> recovery: percentage of CO<sub>2</sub> captured per voyage, year and rated (per operating point).
- CO<sub>2</sub> product purity and state of storage
- Power consumption requirements for CCS system operation
- Heat consumption requirements for CCS system operation
- Consumption of resources for CCS system operation
- CCS plant dimensions

# Definition of process requirements & specifications

## Maritime case specifications (Task Leader: DNV)

Comparative assessment of the different solvent classes for CO<sub>2</sub> capture using on board KPIs\*

	Physical Solvents	Primary Amines	Secondary Amines	Tertiary Amines	Sterically Hindered Amines	Amine Blends	Phase-Change Solvens	Ionic Liquids	Salts	Ammonia	Seawater	Degree of Criticality
Maturity	5	5	5	4	4	3	1	1	4	4	1	I
Compactness	3	3	3	3	3	4	4	4	3	3	2	I
Energy penalty	3	2	3	3	3	4	5	5	4	4	4	I
CO <sub>2</sub> loading	2	3	3	4	4	5	5	5	3	3	1	I
Health and safety	3	3	3	3	3	3	3	4	4	2	5	I
Operability range	4	4	4	3	2	4	3	4	4	3	3	II
Impurity tolerance	2	3	3	3	4	3	3	4	4	4	4	II
OPEX	4	2	2	3	3	2	2	2	4	4	5	II
Other consumables	4	4	4	4	4	4	4	4	2	4	2	II

(\* ) Color coding is a measure of the quality of the KPI

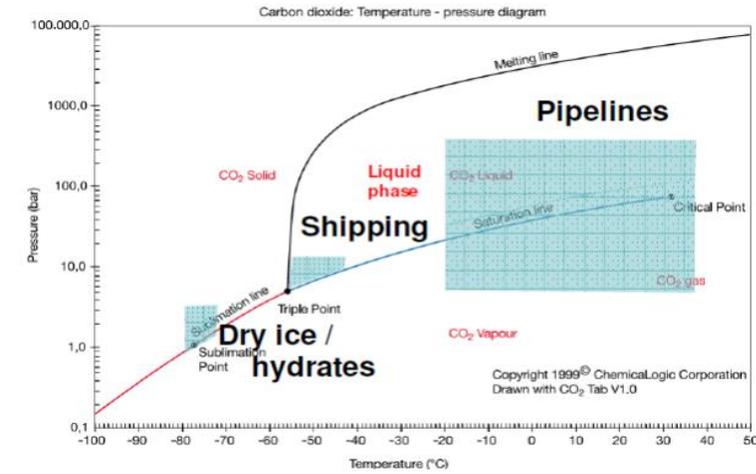
Green (5): good, Light green (4): medium-good, Yellow (3): medium, Orange (2): medium-bad, Red (1): bad

Damartzis, T., et al, Solvents for membrane-based post-combustion CO<sub>2</sub> capture for potential application in the marine environment, 2022, Appl. Sci. 2022, 12

# Definition of process requirements & specifications

## Maritime CO<sub>2</sub> storage options (Task Leader: DNV)

### Carbon storage options

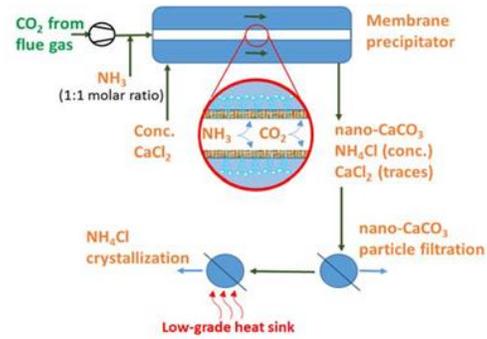


TNO (2016) Transportation and unloading of CO<sub>2</sub> by ship - a comparative assessment, WP9 Final report CO<sub>2</sub> shipping

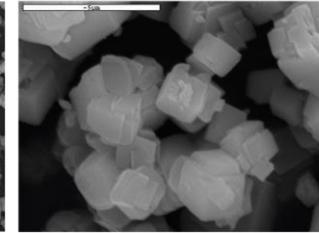
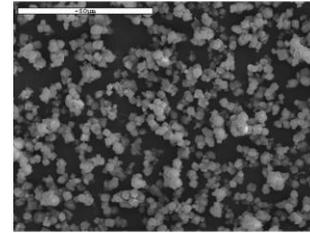
### Carbon Storage Challenges

- Limited space onboard (cf. solidification)
- Sea motions (cf. liquefaction)
- Low CO<sub>2</sub> fractions
- Purity levels of the CO<sub>2</sub> product
- Seakeeping

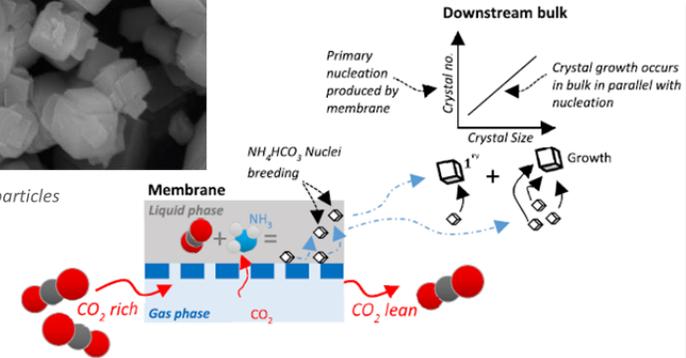
### Carbon mineralization



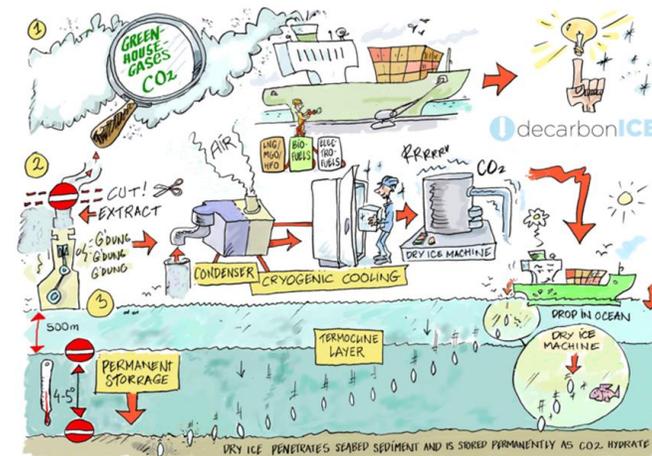
Scanning Electron Microscopy – SEM



Homogeneous cubic Calcite particles



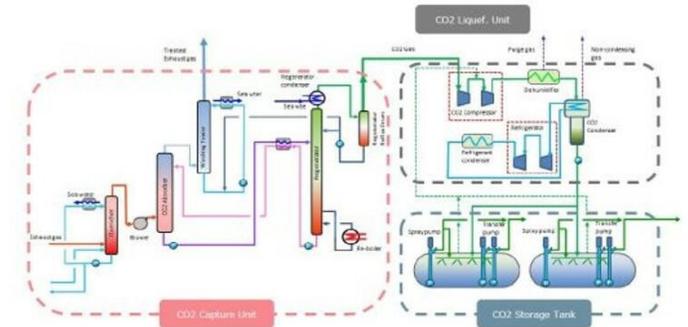
### Conversion to hydrates



### Liquefaction

System Composition of CCS on board

- ◆ Liquid Amine absorption method CO<sub>2</sub> capture unit
- ◆ Liquefaction unit
- ◆ Storage tank



# Materials development

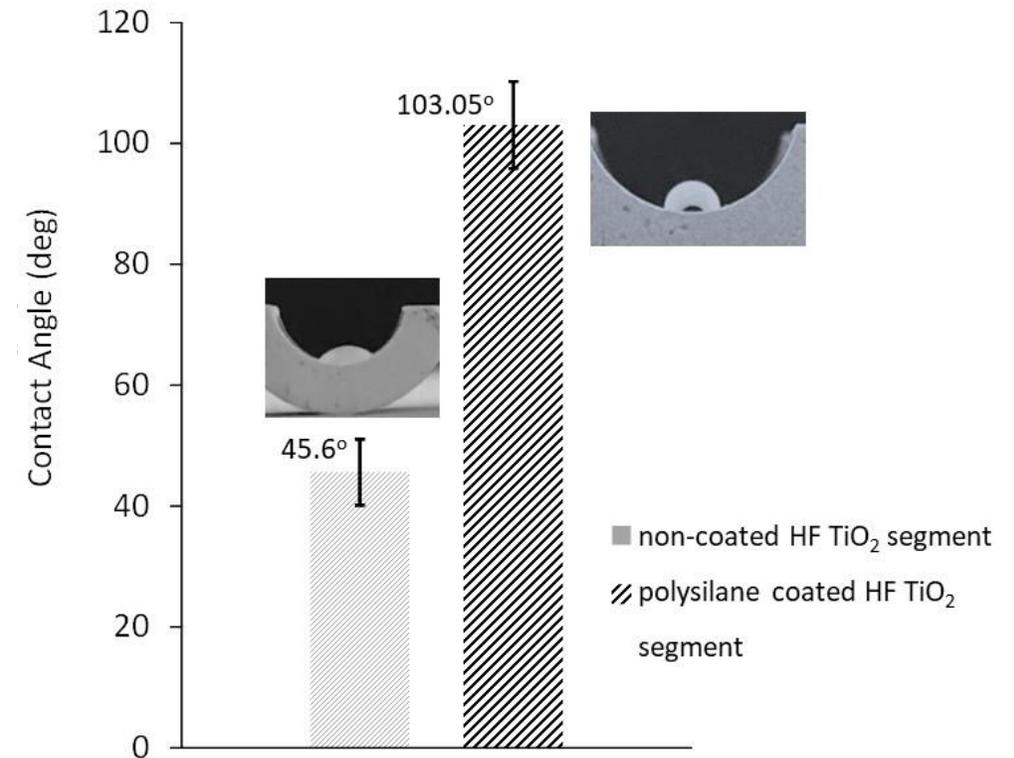
## Ceramic membranes

In membrane gas liquid contactor, gas shall permeate through open pores, but liquid should never permeate through pores:

- Hydrophobic membranes
- High Liquid Entry (water) Pressure

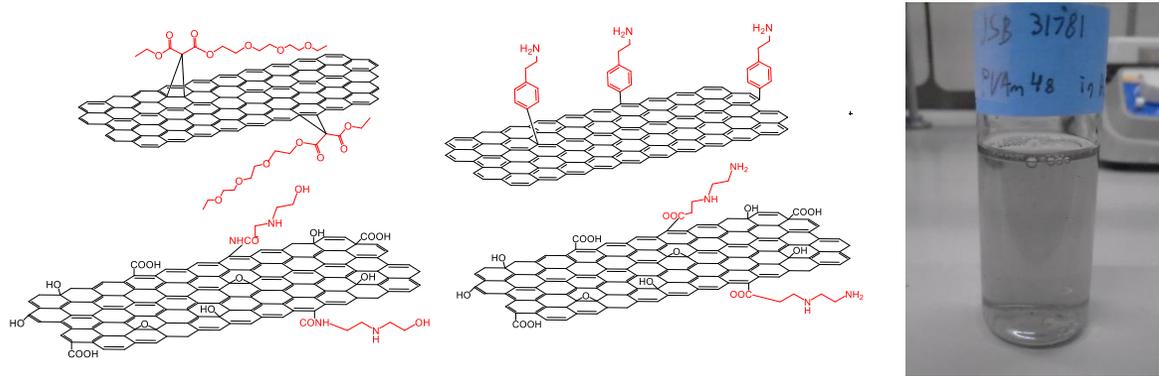


- ✓ Membranes of highest contact angle in water → **extremally hydrophobic**
- ✓ Membranes of LEP up to 12bar → **Perfect membranes for membrane contactors, M2 achieved !**
- ✓ Outstanding action: Scaling-up of membrane preparation

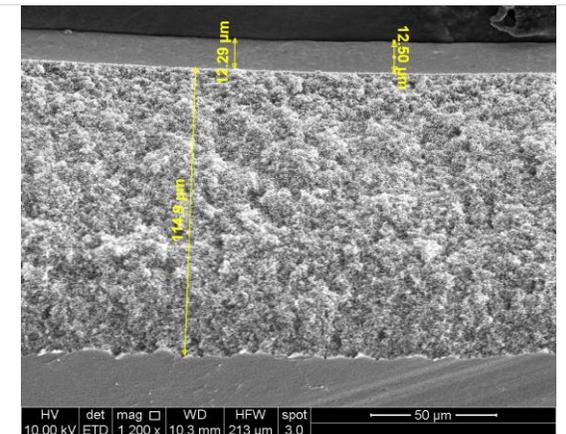
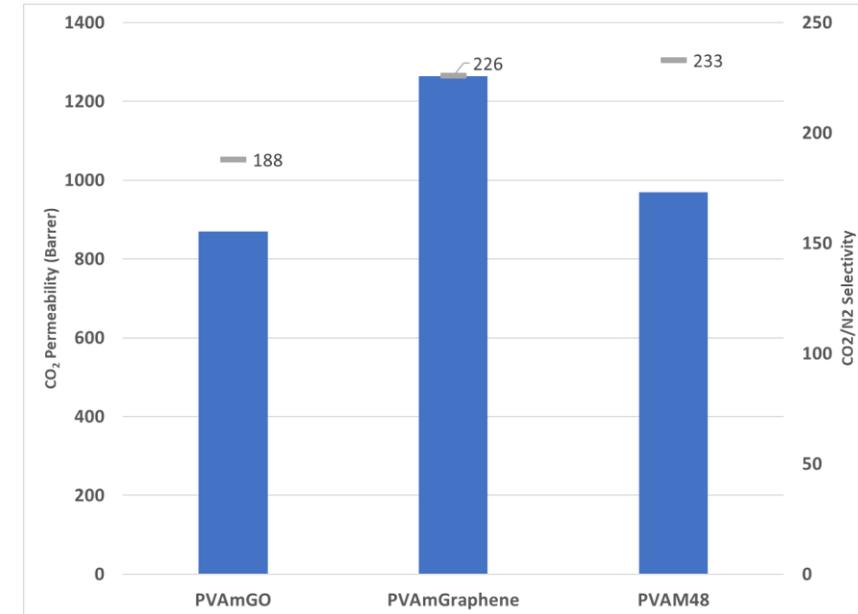


# Materials development

## Polymeric-based membranes (MMM) preparation and modification



- Graphene of different surface modification → dispersible in different solvents (ethanol)
- Polymeric membranes of excellent CO<sub>2</sub>/N<sub>2</sub>-selectivity (230!) and CO<sub>2</sub>-permeance
- Graphene containing membranes (MMM) of same excellent CO<sub>2</sub>/N<sub>2</sub>-selectivity (230) and by 30% increased CO<sub>2</sub>-permeance
- Perfect membranes for membrane permeators, M3 achieved
- Outstanding action: Preparation of MMM as thin layer on porous support



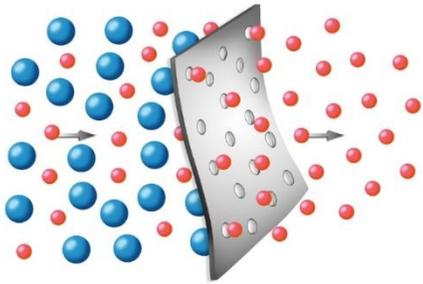
# Membrane Preparation and Characterization

## Development of Advanced 3D Printed Membranes

MIS 5136520/KMP6-0232019

Start: 08-10-2021

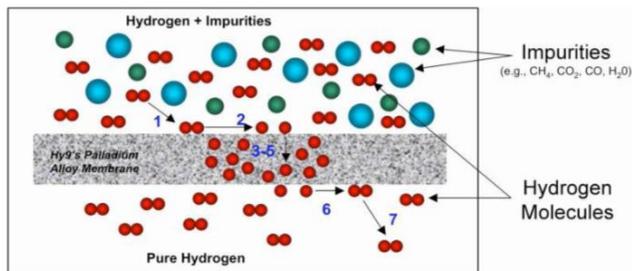
### POLYMERIC



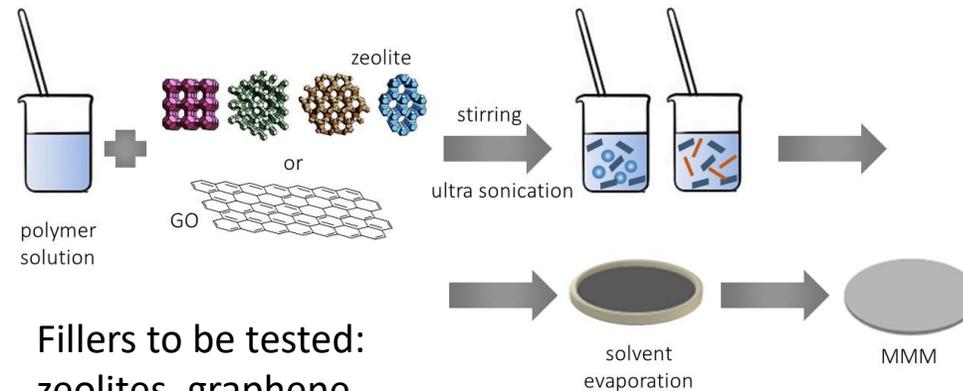
### MIXED MATRIX

Mixed matrix membrane materials (MMM) Heterogeneously structured membranes combine individual advantages of matrices (e.g. polymers) and fillers (e.g. zeolites) and may offer great benefits in tailoring membrane separation efficiency.

### METALLIC



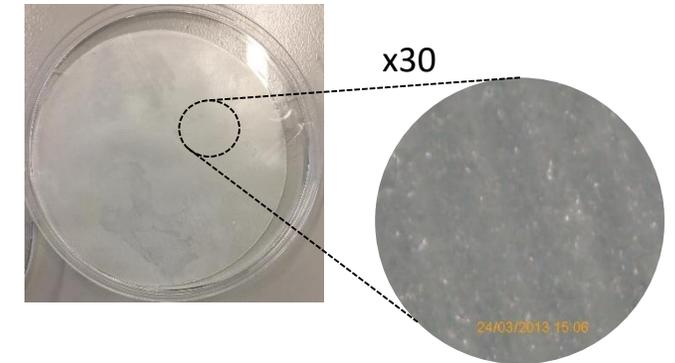
Adopted by Al-Hadeethi et al (2013)



Fillers to be tested:  
zeolites, graphene,  
graphene oxide, CaO

### Preliminary results

Polycarbonate-like membrane  
3D printed by VisiJet CR-CL

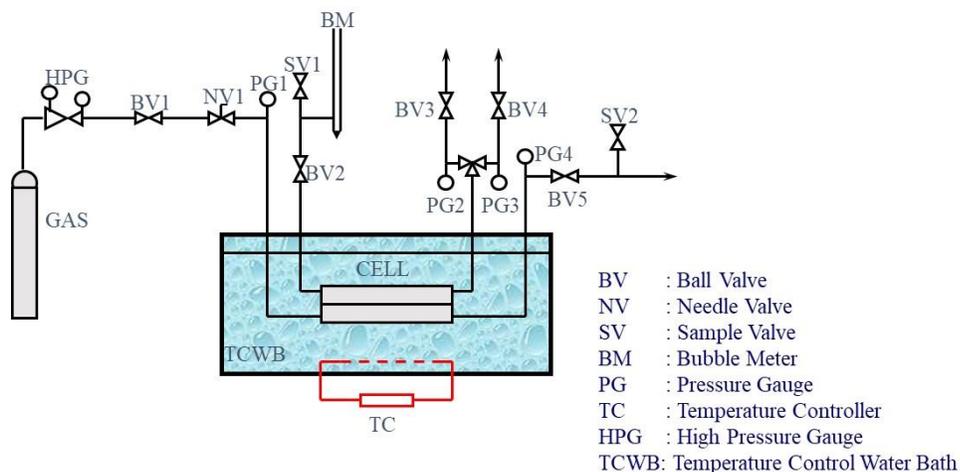


Permeability of CO<sub>2</sub>, O<sub>2</sub>,  
N<sub>2</sub>, He >1E+04 barrer →  
Low Selectivity

# Membrane Preparation and Characterization

## Permeability measurement

Constant pressure (isobaric) gas permeation system to quantify pure gases' permeances (e.g. CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, Ar, etc.)



- ✓ Samples: Polymeric thin films in the form of discs (diameter ~6 cm)
- ✓ Operating principle: Variable volume method (Apply a pressure gradient and measure gas flow)

*\*Different sample holders and setups can be considered upon request*

The TEESMAT case



# Experimental lab-scale test campaign

**Aim:** to consolidate activities performed in **WP1** & **WP2** and proceed with the experimental evaluation of membranes/processes, in order to create data banks for **component and system models' validation, verification and optimization (WP4)**.

## Experimental evaluation of membranes materials

- Investigation of different membrane materials (polymeric, ceramic, carbon, etc.) and modules

## Initial evaluation of membranes and process performance

- Main membrane characteristics (e.g. CO<sub>2</sub> permeance and selectivity, membrane mass transfer resistance, etc.)
- Investigation of various process and operating parameters (e.g. gas compositions, solvents, temperature, pressure, CO<sub>2</sub> recovery, stage cut, pressure ratio, L/G ratio, etc.).

## Ashore pilot testing of the marinized units

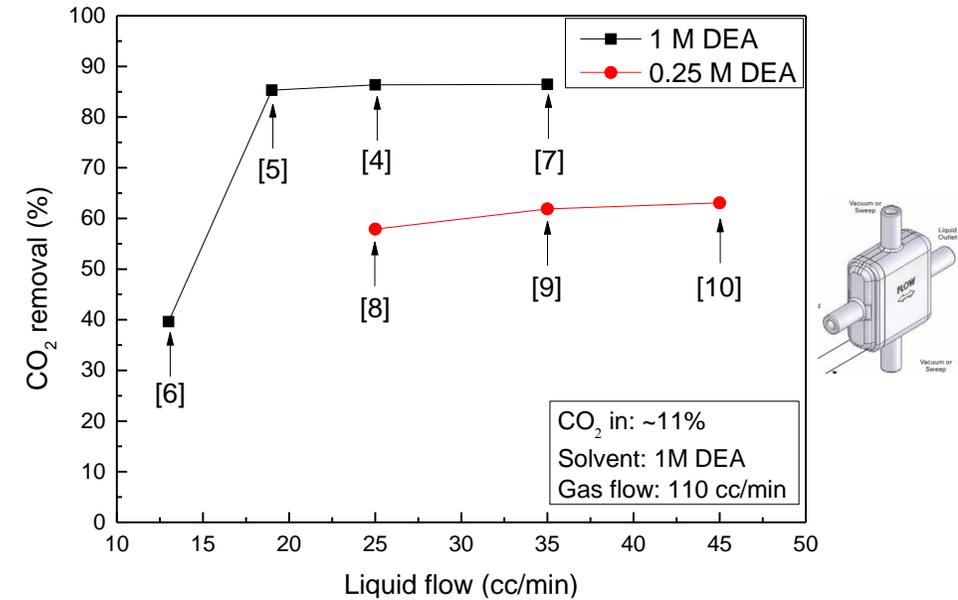
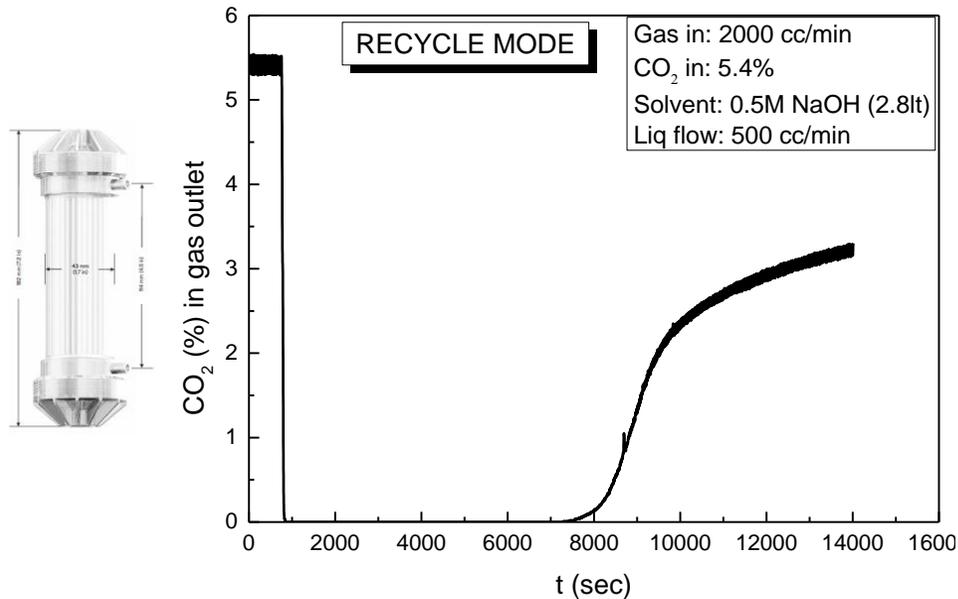
- Prototype pilot unit to assess the performance at simulated process conditions and demonstrate the CO<sub>2</sub> capture potential of the developed systems to relevant stakeholders.

# Experimental lab-scale test campaign

## Membrane contactors

### Initial evaluation of membrane performance (Task Leader: DBI)

#### Membrane CO<sub>2</sub> capture results with polymeric membrane modules



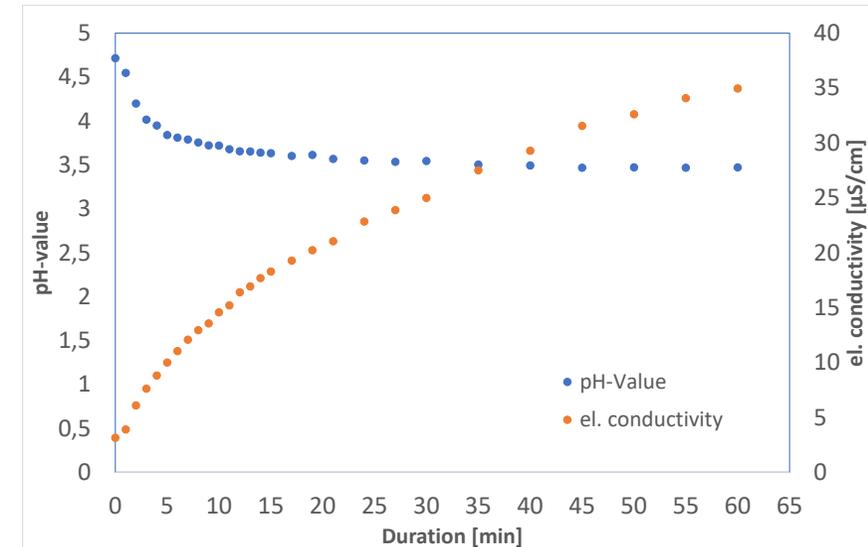
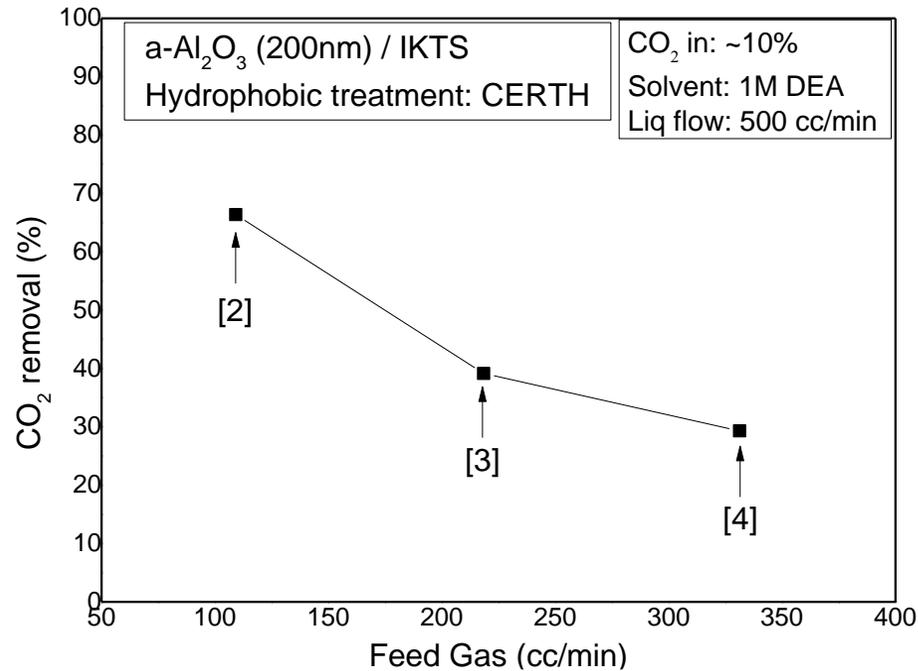
- ✓ Different operation modes (once-through vs recycling ) and various parameters (i.e. CO<sub>2</sub> concentration, solvent, G/L ratio) were tested
- ✓ Complete CO<sub>2</sub> removal for more than 2h of operation using 2.8 lt of 0.5M NaOH or very diluted DEA, in recycling mode

- ✓ 5-10 times higher treating capacities were achieved in once through mode
- ✓ System design and optimization is needed to reserve the high performance by controlling the addition of fresh solvent and the removal of spent

# Experimental lab-scale test campaign

### Initial evaluation of membrane performance (Task Leader: DBI)

Membrane CO<sub>2</sub> capture results with ceramic membrane modules



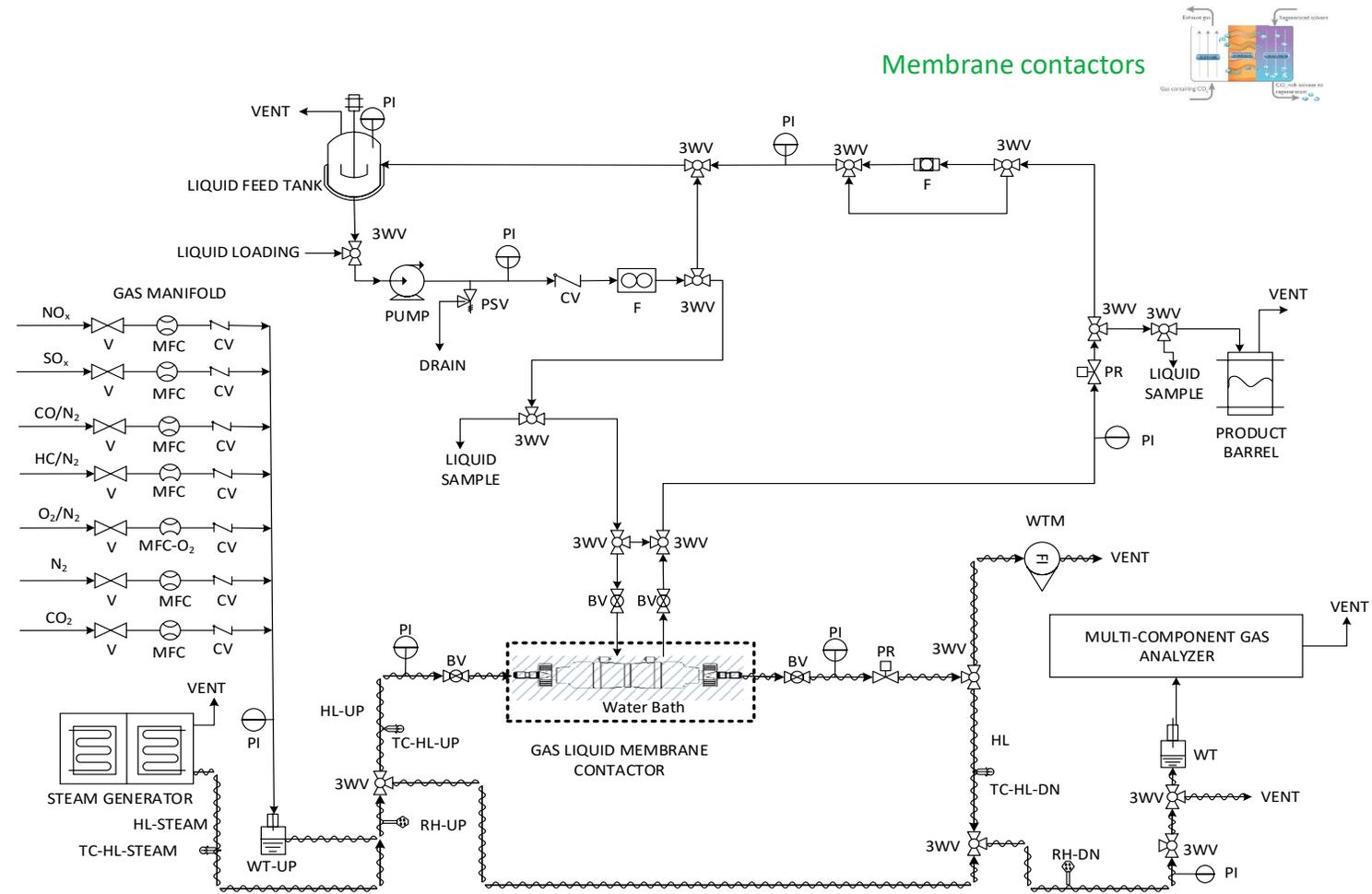
- ✓ Very high treating capacities achieved
- ✓ CO<sub>2</sub> removal efficiencies up to 60% at treating capacities of  $\sim 1.3 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$

- ✓ Very stable operation for several hours without wetting or performance loss
- ✓ CO<sub>2</sub> removal efficiencies at low T (10°C) with deionized and degassed water

# Experimental pilot test campaign

*Ashore pilot testing of the marinized units (Task Leader: CERTH)*

A prototype pilot unit for gas Permeator/membrane Contactor applications is already built at CERTH to evaluate separation systems developed within the project, at simulated process conditions: flowrates, gas composition etc.



# Experimental pilot test campaign

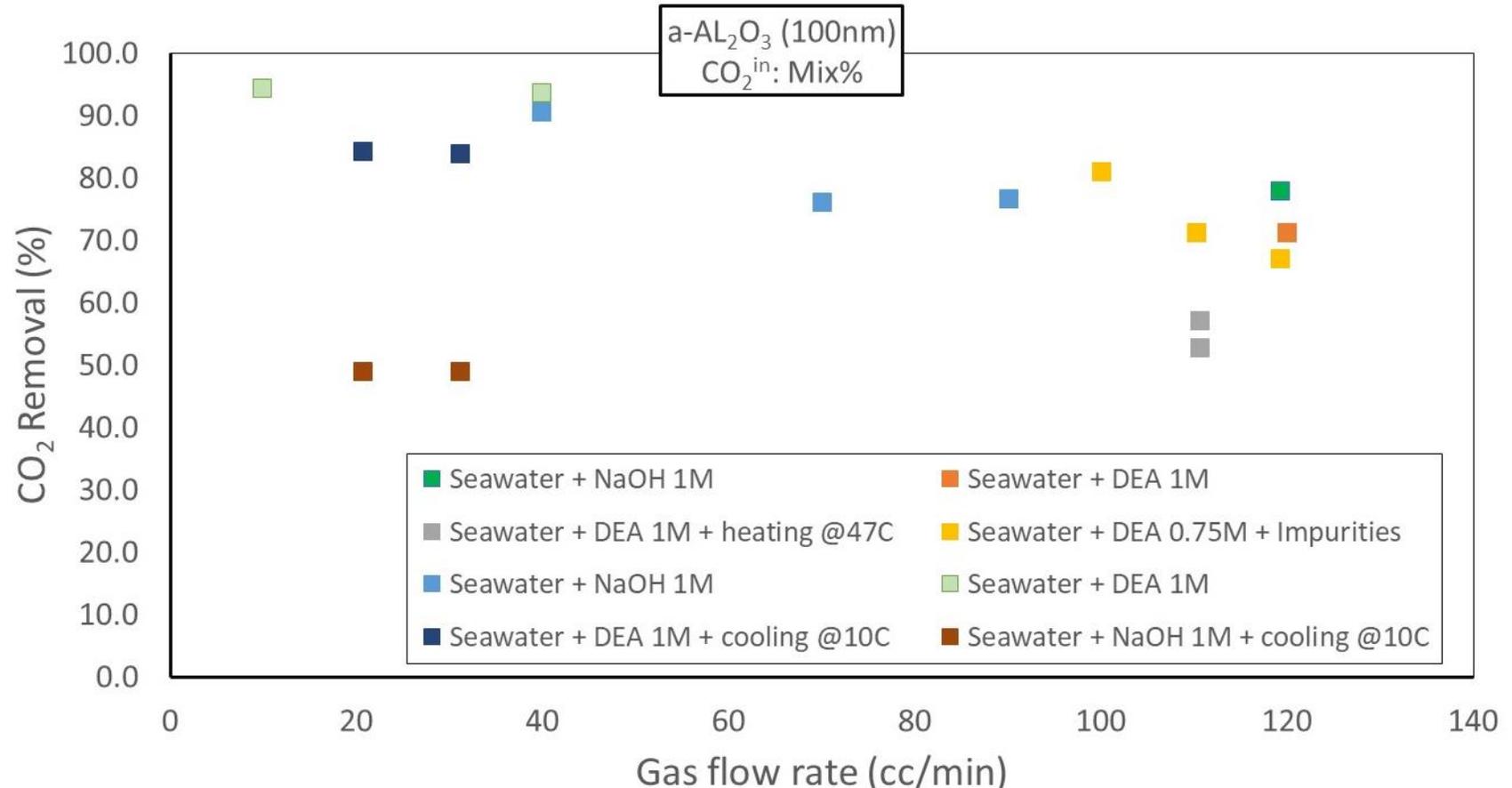
Membrane contactors



Membrane CO<sub>2</sub> capture results with ceramic membrane modules, simulated marine engine flue gases and seawater-based solvents

FLUEGAS	
CH <sub>4</sub> (ppmv)	190.00
O <sub>2</sub>	13.70 %
CO <sub>2</sub>	5.9 %
CO (ppmv)	60
NO <sub>x</sub> (ppmv)	1580
SO <sub>2</sub> (ppmv)	125
N <sub>2</sub>	balance

SYNTHETIC SEAWATER COMPOSITION	
H <sub>2</sub> O (% w/w)	96.5
NaCl (% w/w)	2.7192
MgCl <sub>2</sub> (% w/w)	0.2447
MgSO <sub>4</sub> (% w/w)	0.3305
CaCl <sub>2</sub> (% w/w)	0.1141
KCl (% w/w)	0.0725
NaHCO <sub>3</sub> (% w/w)	0.019



Asimakopoulou A., et al, Experimental evaluation of CO<sub>2</sub> capture with gas-liquid membrane contactors and seawater-based solvents in maritime applications, Membranes 2022, submitted

# Process modelling

## Transport phenomena modelling (Task Leader: NETL)

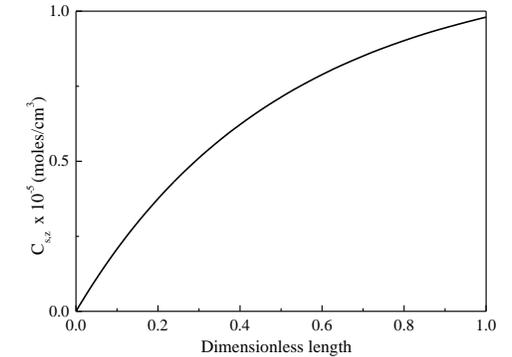
### Coupled gas-liquid membrane process model with solution thermodynamics

#### Model assumptions (Pantoleonos et al., 2010, 2017)

- Steady state, isothermal
- 2D model, fully developed, laminar flow in the lumen (fiber)
- Gas (CO<sub>2</sub>) in the lumen side, reaction in the shell side with the liquid solvent (e.g. MEA, DEA, NaOH, Seawater etc)
- Reaction (example):  $\text{CO}_2 + 2\text{RNH}_2 + \text{H}_2\text{O} = \text{RNH}_3^+ + \text{RNHCOO}^-$  (R = HOCH<sub>2</sub>CH<sub>2</sub>) (Aspen Plus contribution)

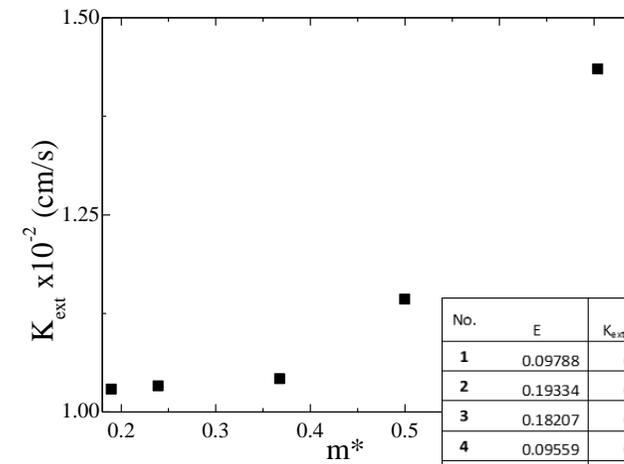
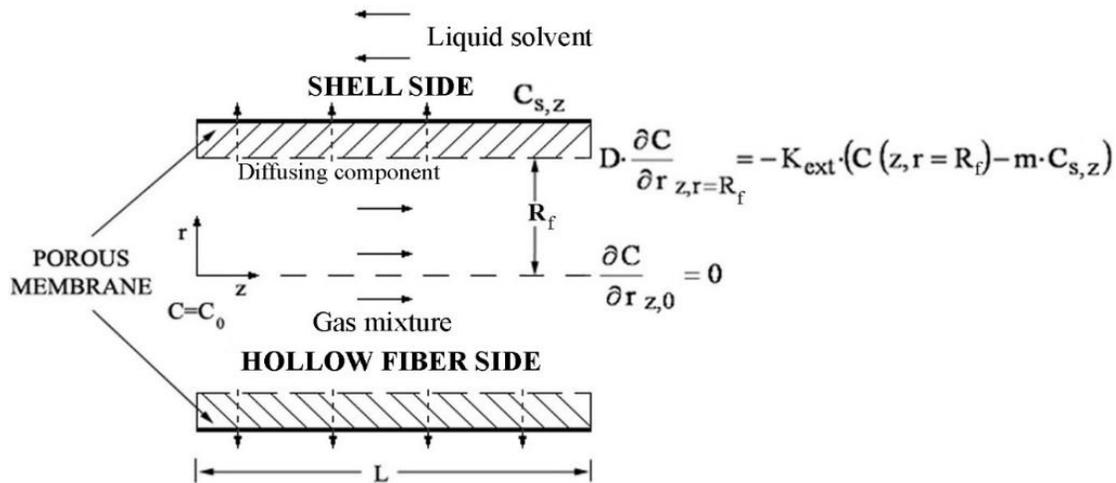
### Computational methodology

- Solution thermodynamics in the presence of electrolytes and other species



Shell-side concentration of CO<sub>2</sub>-related species

- Estimation of overall mass transfer coefficient  $K_{ext}$  from MemCCSea experimental data (WP3)

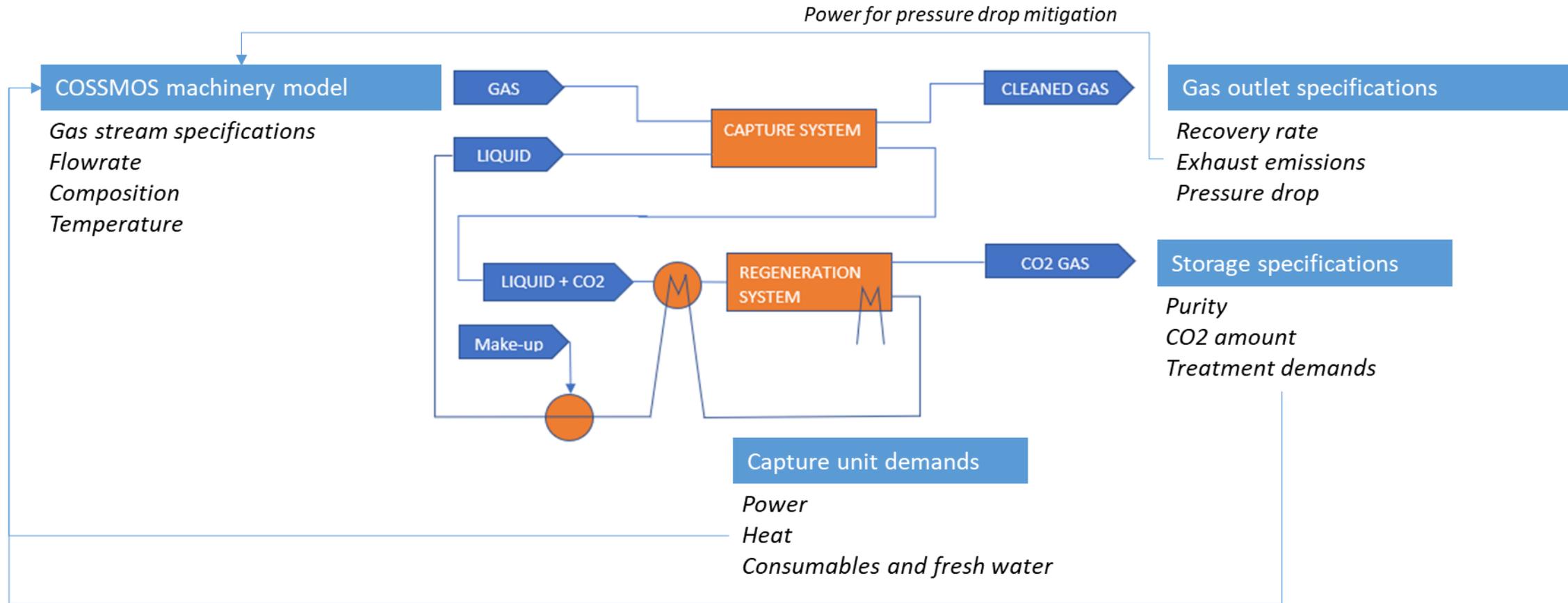


No.	E	$K_{ext}$ (cm/s)	$Sh_w$	M	$m^*$	$H_{CO_2}$ (mol/cm <sup>3</sup> ) <sup>*</sup>	$z^*$
1	0.09788	0.01029	1.600x10 <sup>-3</sup>	0.12094	0.18945	3.582x10 <sup>-5</sup>	222.
2	0.19334	0.01033	1.615x10 <sup>-3</sup>	0.23519	0.23922	3.648x10 <sup>-5</sup>	544.
3	0.18207	0.01042	1.620x10 <sup>-3</sup>	0.22498	0.36774	3.582x10 <sup>-5</sup>	567.
4	0.09559	0.01143	1.786x10 <sup>-3</sup>	0.11628	0.49979	3.648x10 <sup>-5</sup>	214.
5	0.06827	0.01435	2.242x10 <sup>-3</sup>	0.08305	0.70390	3.648x10 <sup>-5</sup>	109.

# Process modelling

*Model-based assessment and optimization of the marinized system (Task Leader: DNV)*

## Model Connectivity definition for the CCS unit (COSSMOS)



# System and performance assessment

## Operating scenarios to achieve 90% or higher CO<sub>2</sub> capture efficiency

Preliminary estimation of space and energy requirements for an on-board membrane capture system

		Without Solvent regeneration		
		Confident	Basic	Safe
Solvent Flow Rate per module (m <sup>3</sup> /h)		70	70	70
Liquid to Gas mass ratio (kg/kg)		2	3	6
# of modules		4	5	10
Power consumption (kW) (only for liquid pumping into the module system)		7.8	9.7	19.5
Space Required (only for module set up) <i>L (m) x D (m) x H (m)</i>	In line	2.38 m <sup>3</sup> 3.3x0.6x1.2	3.03 m <sup>3</sup> 4.2x0.6x1.2	6.27 m <sup>3</sup> 8.7x0.6x1.2
	Parallel	2.7 m <sup>3</sup> 1.5x1.5x1.2	4.32 m <sup>3</sup> 2.4x1.5x1.2	9.5 m <sup>3</sup> 3.3x2.4x1.2

### Assumptions

- Exhaust gas flow rate 110 t/hr
- Exhaust gas CO<sub>2</sub> concentration: 15% b.v.
- No solvent regeneration
- Solvent efficiency similar to an aqueous MEA solution 30% w/w.

For solvent regeneration the liquid to gas mass ratio will increase. This will lead to a proportional increase of membrane modules.

*What is it?* Systematic review of possible causes & consequences of hazardous events

*Typical application areas:* HAZID investigations are commonly applied to offshore installations

*Why?* Hazard assessment: the most important step in Quantitative Risk Assessment (QRA)

- Gain appreciation of range & magnitude of hazards
- Suggest prevention, mitigation, control
- Improvement of concepts → **Risk Management**

## Approach

**Assemble team of experts in**

- **Ships in operation: tankers & chemical carriers**
- **Systems approval**
- **Technology (CCS) qualification**
- **Process modelling & simulation**

**Systematic discussion through the system's modules & operations**

**Completion of a HAZID work sheet: Hazard, Causes, Consequences, Safeguards & remarks**

# Key Achievements

- A **case ship** for (virtual) membrane-based carbon capture system integration has been **selected** and **operating conditions and exhaust gas characteristics defined** (in close collaboration with **EURONAV**)
- **Selection, development and screening of membrane** (polymeric+graphene) & **solvents** (seawater, amine-based, metal hydroxides) for gas-liquid membrane capture.
- **Ceramic membrane** surface modification for **increased hydrophobicity** completed and evaluated.
- A **prototype pilot unit for ashore membrane testing** is being developed and **test protocols** for the experimental evaluation have been **defined**.
- **Process model for mass and energy balances** for membrane-based capture module assembly on-board ships scale-up.
- ✓ Recovery of the **main engine CO<sub>2</sub> emissions greater than 90%**
- ✓ **A 10-fold reduction of system volume** compared to a conventional amine-based scrubbing system.

## Still pending:

➤ reduction of operating costs greater than 25%

➤ Overall CO<sub>2</sub> emissions reduction (including added emissions by the capture plant and utilities greater than 50%)

# Dissemination

## MemCCSea participation in 85<sup>th</sup> Thessaloniki International Fair, 11-19.09.2022, Thessaloniki, Greece

MemCCSea Project presentation in the 85<sup>th</sup> Thessaloniki International Fair through a virtual reality tool 'Ship VR'.



## Round Table Discussion on Novel CCS Technologies for Industry and Marine Transportation

**ΕΚΕΤΑ**  
ΕΘΝΙΚΟ ΚΕΝΤΡΟ  
ΕΡΕΥΝΑΣ & ΤΕΧΝΟΛΟΓΙΚΗΣ  
ΑΝΑΠΤΥΞΗΣ

**AEO HELEXPO**

Το Ινστιτούτο Χημικών Διεργασιών & Ενεργειακών Πόρων (ΙΔΕΠ) του Εθνικού Κέντρου Έρευνας & Τεχνολογικής Ανάπτυξης (ΕΚΕΤΑ)

σας προσκαλεί σε  
Συζήτηση Στρογγυλής Τραπέζης  
με θέμα

«Καινοτόμες τεχνολογίες δέσμευσης & αξιοποίησης CO<sub>2</sub> και άλλων αέριων ρύπων, σε εφαρμογές βιομηχανικού ενδιαφέροντος, στην ενέργεια και τη ναυτιλία»

MemCCSea Σάββατο, 18 Σεπτεμβρίου 2021, 19.00 μ.μ.  
ΔΕΘ Helexpo – Περίπτερο 7, Stand 3, ΓΓΕΚ

**PUREHY**

**Ομιλητές:**

- Γιώργος ΔΗΜΗΤΡΙΑΔΗΣ**  
Μηχανολόγος Μηχανικός, Τεχνικός Διευθυντής, CaO HELLAS
- Γιάννης ΚΟΥΓΙΑΣ**  
Δρ Πολιτικός Μηχανικός, Regulatory & Business Analysis Ma
- Γιώργος ΔΗΜΟΠΟΥΛΟΣ**  
Δρ Ναυπηγός Μηχανικός, Principal Research Engineer, DNV
- Θεμιστοκλής ΣΦΕΤΣΑΣ**  
Χημικός, Technical Manager, Qlab
- Γιώργος ΚΑΡΑΓΙΑΝΝΑΚΗΣ**  
Δρ Χημικός Μηχανικός, Κύριος Ερευνητής, ΕΚΕΤΑ
- Πάνος ΣΕΦΕΡΛΗΣ**  
Δρ Χημικός Μηχανικός, Καθηγητής, ΑΠΘ

Την συζήτηση θα συντονίσει ο **Γιώργος ΣΚΕΥΗΣ**, Δρ Μ  
Κύριος Ερευνητής, ΕΚΕΤΑ

Accelerating CCS Technologies | ΓΓΕΚ | ΕΠΑΝΕΚ 2014-2020 | ΕΠΙΧΕΙΡΗΣΙΑΚΟ ΠΡΟΓΡΑΜΜΑ ΑΝΤΑΓΩΝΙΣΤΙΚΟΤΗΤΑΣ, ΕΡΕΥΝΑΣ ΚΑΙ ΚΑΙΝΟΤΟΜΙΑΣ



# Project Overview

Project duration  
1/11/2019 – 30/4/2022 (30M)  
*Extension to 31/10/2022*

Budget  
1.98 M€



<http://memccsea.certh.gr>