

**VSL**

**National  
Metrology  
Institute**

## **MetCCUS project overview**

**Seminar Metrology Support for Carbon  
Capture Utilization and Storage**

**Iris de Krom**

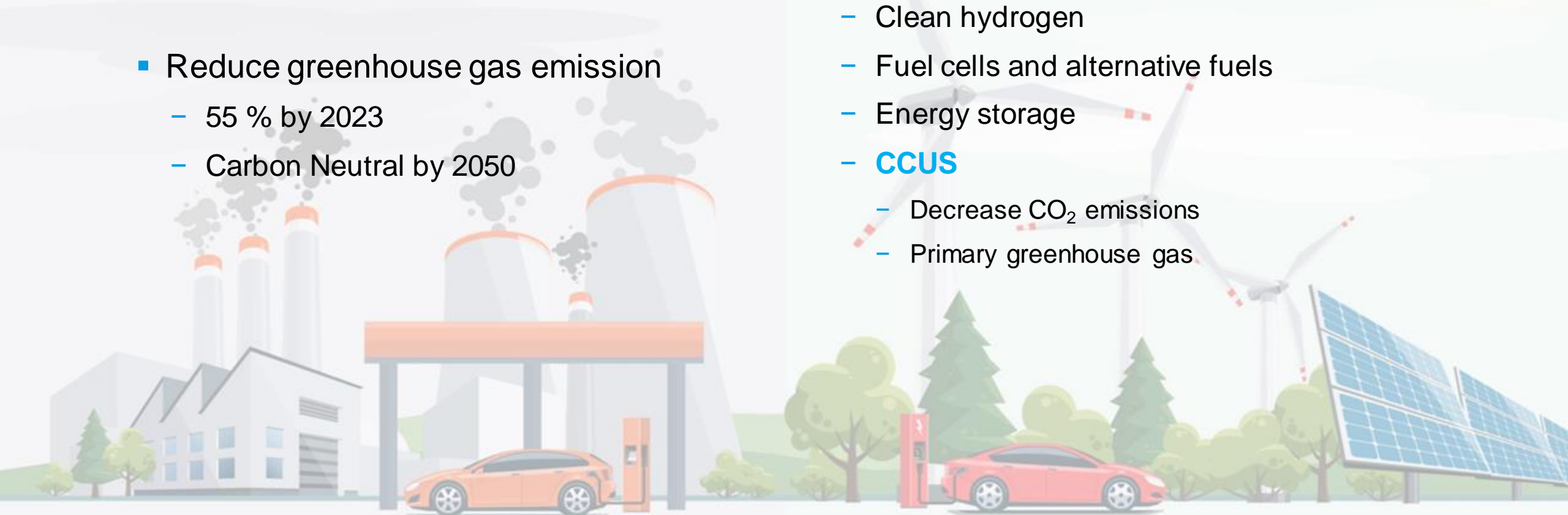
**26 October 2023 – Online**



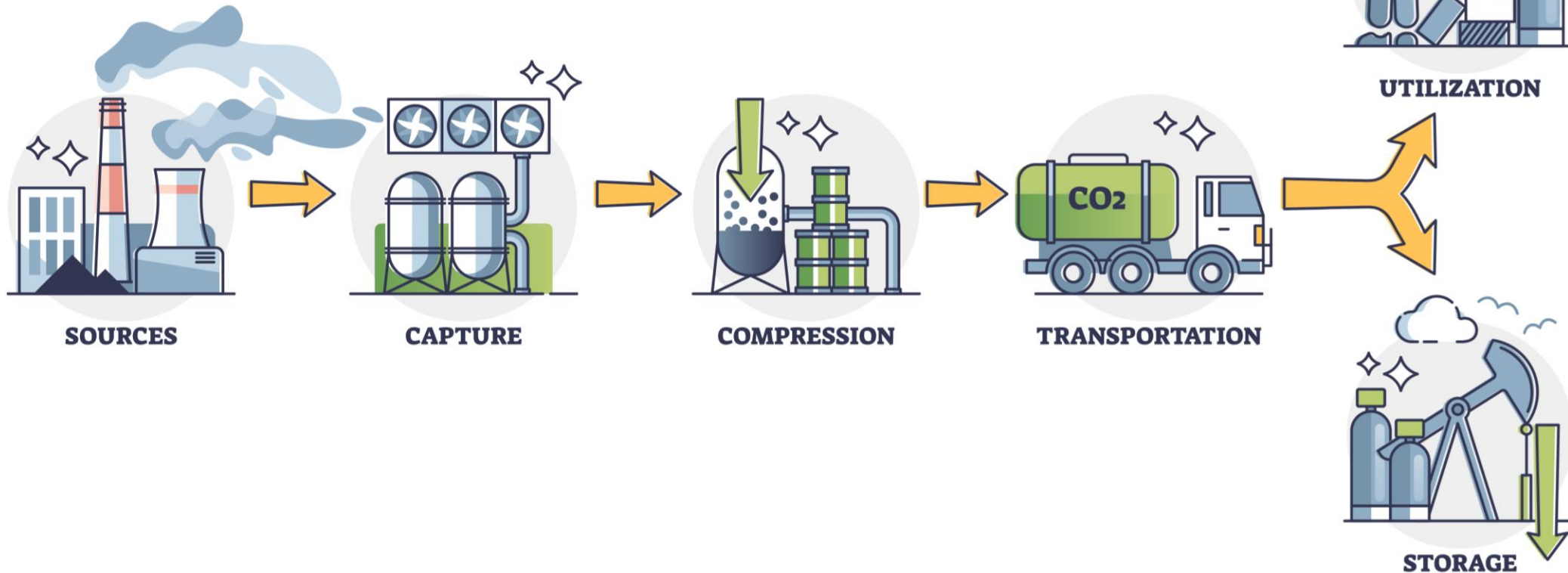
**METCCUS**

# Carbon Capture Utilization and Storage (CCUS)

- Climate change
- Reduce greenhouse gas emission
  - 55 % by 2023
  - Carbon Neutral by 2050
- European Green Deal → Clean Energy
  - Clean hydrogen
  - Fuel cells and alternative fuels
  - Energy storage
  - **CCUS**
    - Decrease CO<sub>2</sub> emissions
    - Primary greenhouse gas



## CARBON CAPTURE





# Metrology support for CCUS

METROLOGY PARTNERSHIP



- 1 October 2022 – 30 September 2025
- 21 participants



Justervesenet



RUHR UNIVERSITÄT BOCHUM



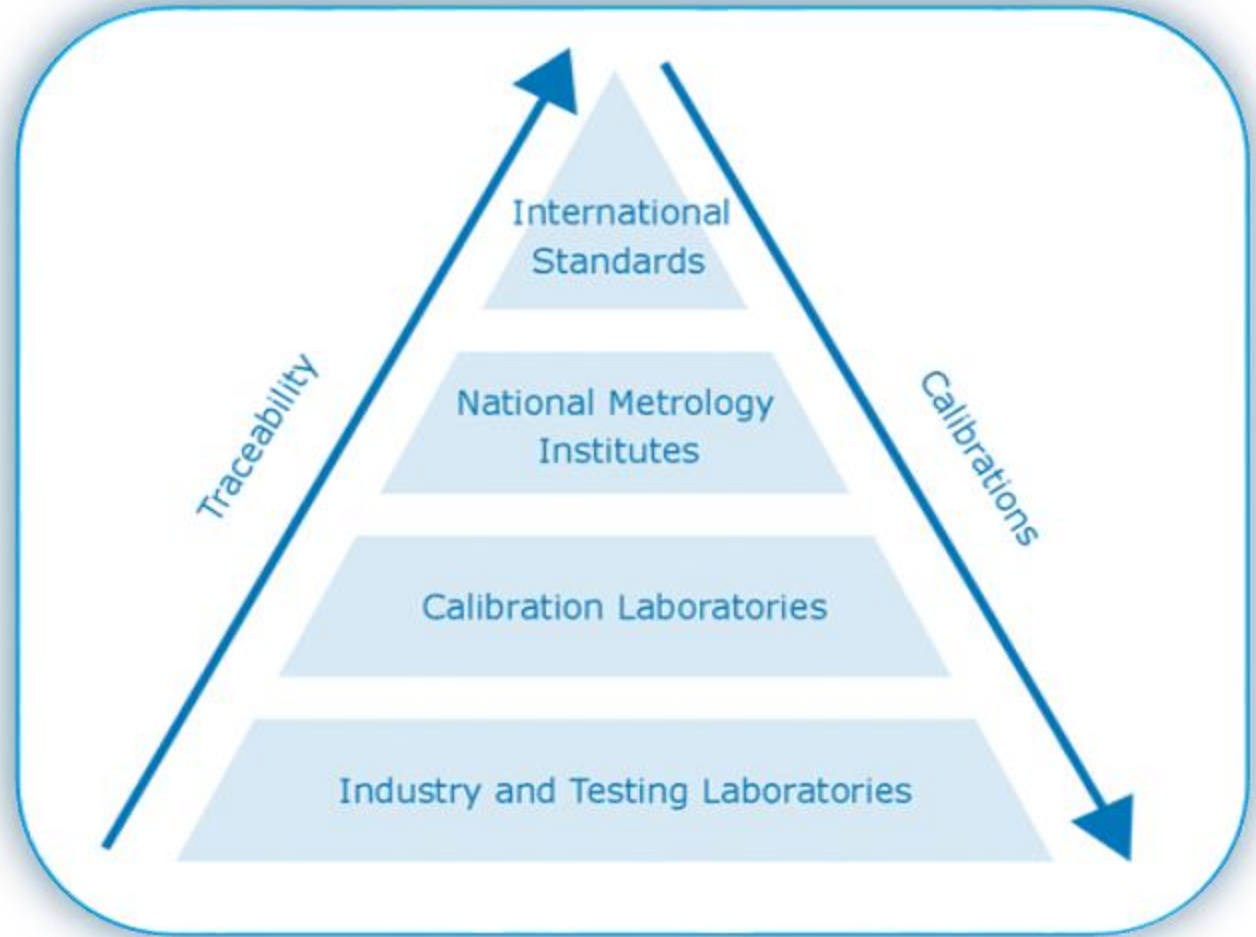
UNIVERSITA DEGLI STUDI DI TORINO



Universidad de Valladolid



*"The project has received funding from the European Partnership on Metrology, co-financed by European Union Horizon Europe Research and Innovation Programme and from the Participating States."*



# CCUS measurement challenges

## Flow metering



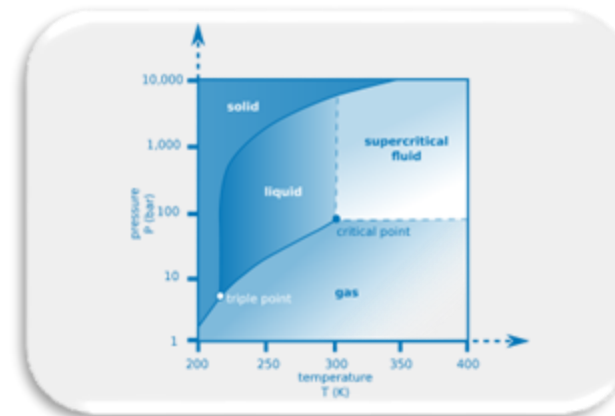
## Emission monitoring



## Chemical metrology



## Physical properties



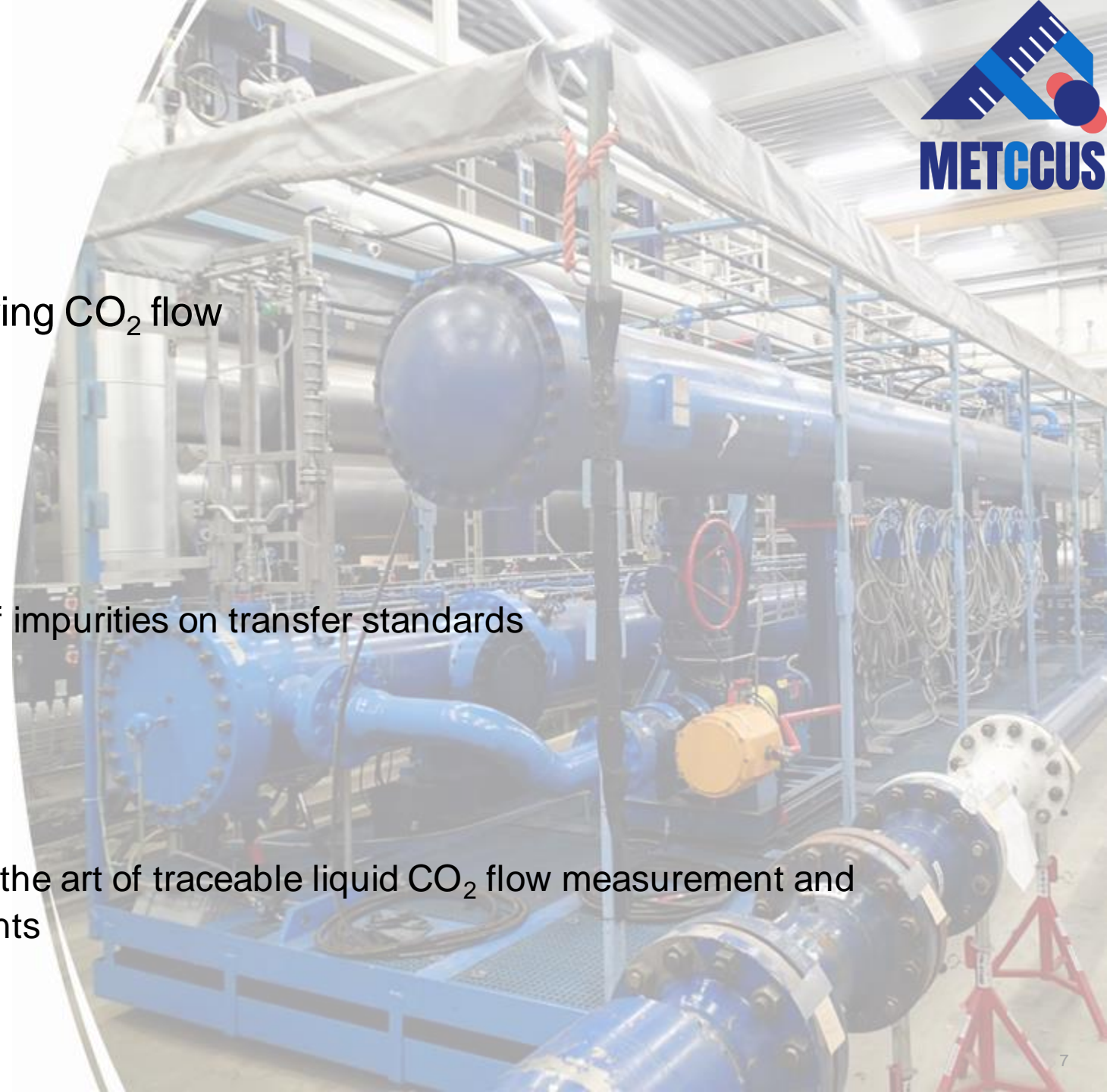
## Flow metering

### Gas-flow

- Metrology infrastructure for monitoring CO<sub>2</sub> flow
  - < 50 m<sup>3</sup>/h and low pressure
  - Up to 400 m<sup>3</sup>/h and higher pressure
- Primary and transfer standards
  - Intercomparison
  - Theoretical investigate the impact of impurities on transfer standards
- Uncertainty 1.5 % - 2.5 %

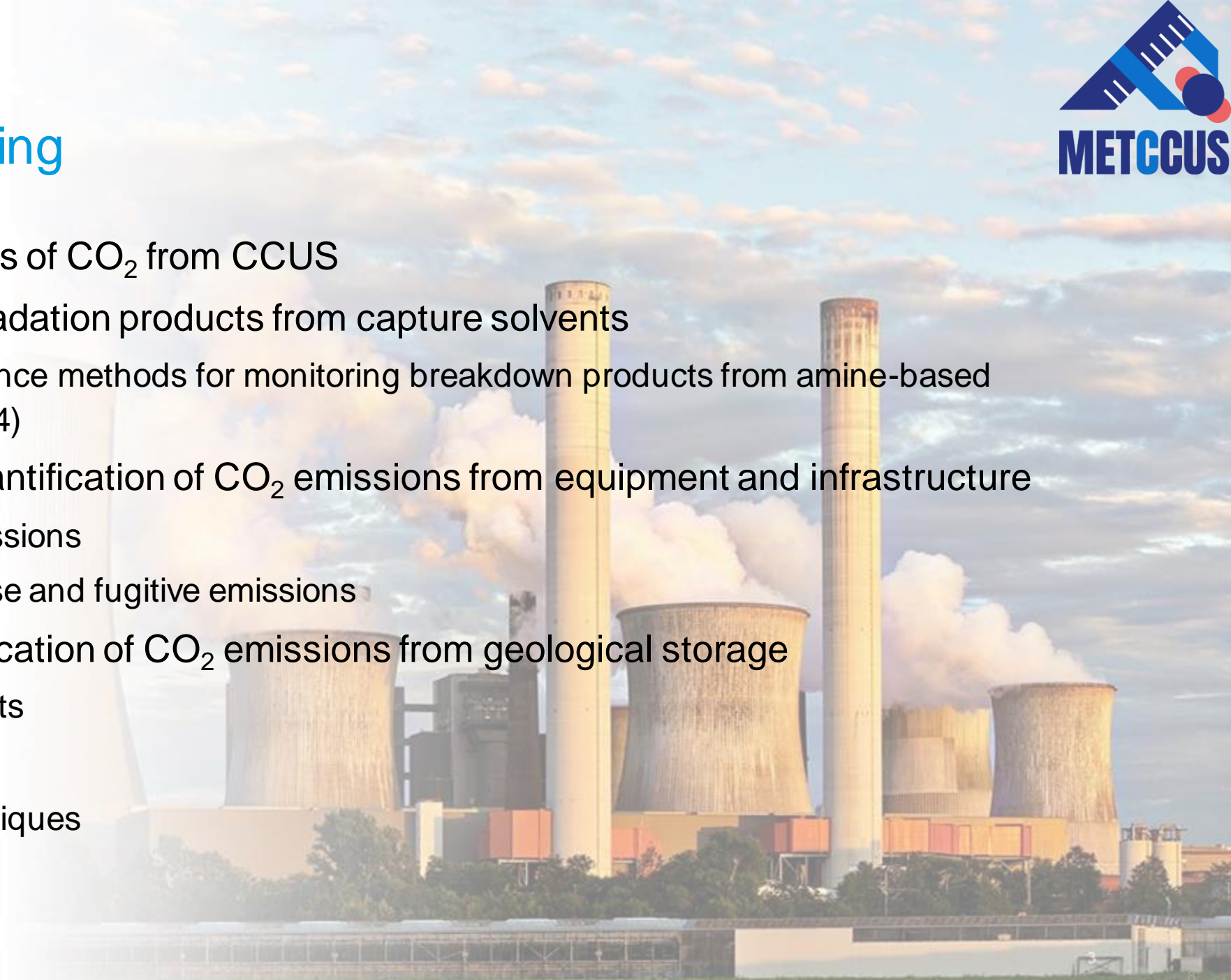
### Liquid flow

- Study to determine the current state of the art of traceable liquid CO<sub>2</sub> flow measurement and liquid CO<sub>2</sub> primary standard requirements



## Emission monitoring

- Atmospheric emissions of CO<sub>2</sub> from CCUS
- Measurement of degradation products from capture solvents
  - First European reference methods for monitoring breakdown products from amine-based solvents (CEN/TC 264)
- Measurement and quantification of CO<sub>2</sub> emissions from equipment and infrastructure
  - Leaks → fugitive emissions
  - Facility scale → diffuse and fugitive emissions
- Detection and quantification of CO<sub>2</sub> emissions from geological storage
  - Isotopic measurements
  - Addition of tracers
  - Use of acoustic techniques



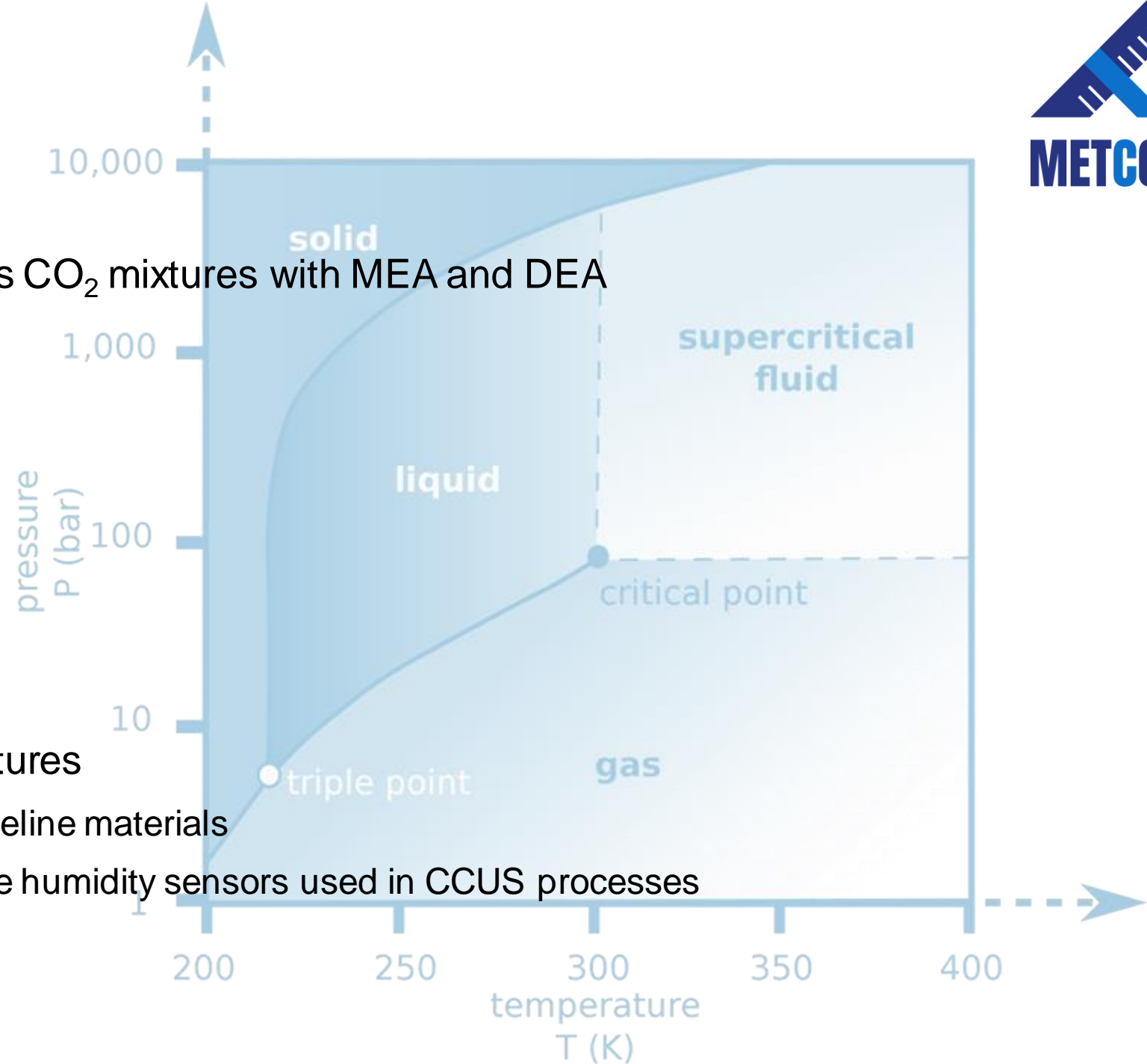


## Chemical metrology

- Primary reference materials for impurities in CO<sub>2</sub>
  - Key impurities e.g.; H<sub>2</sub>O, NO<sub>x</sub>, sulphur compounds, hydrocarbons, alcohols and amines
  - Permanent gases: O<sub>2</sub>, Ar, N<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>
- Material compatibility for CO<sub>2</sub> sampling
- Online CO<sub>2</sub> monitoring
  - Development and validation of online methods
  - Round Robin Test for the measurement of impurities in CO<sub>2</sub>
- Offline analytical methods for CO<sub>2</sub> quality
  - CO<sub>2</sub> capture, transport and storage
  - CO<sub>2</sub> conversion, utilisation and recycling

# Physical properties

- Experimental measurements CO<sub>2</sub> mixtures with MEA and DEA
  - Density
  - Speed of sound
  - Viscosity
  - Heat capacity
- Equation of state models
  - CCUS processes
  - Flow metering
- Monitoring CCUS infrastructures
  - Corrosion testing of CO<sub>2</sub> pipeline materials
  - Calibration method for online humidity sensors used in CCUS processes



## Impact MetCCUS

- Development of
  - Standards and reference materials
  - Calibration and measurement methods
  - Good practice guides
  - Literature reviews & peer reviewed articles
- Support
  - Development of key documentary standards, specifications and regulation
  - Safe and efficient CCUS operation
  - CCUS industry to become carbon neutral and overcome climate change

# Thank you for your attention

- Visit

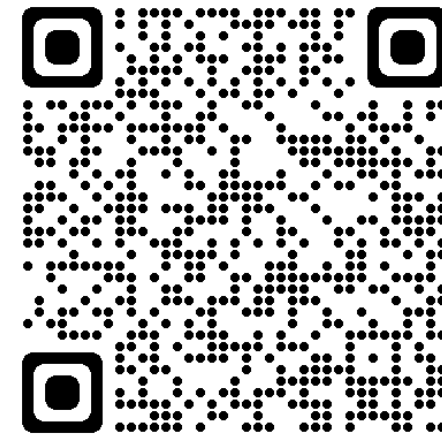
- [www.metccus.eu](http://www.metccus.eu)
- [MetCCUS: Overview | LinkedIn](#)

- Contact

Project coordinator

**Iris de Krom**

idekrom@vsl.nl





# The European Metrology Network for Energy Gases

Annarita Baldan  
EMN Chair

26 October  
MetCCUS seminar



# Drivers

- International:
  - 1.5-degree ambition set under the Paris Agreement
- Europe:
  - Binding target of 55% reduction in GHGs by 2030 compared with 1990
  - Green Deal and “Fit for 55” Package
- Foreseen complex energy mix in the next decades: natural gas, LNG, biogas, biomethane, hydrogen and any future renewable gas



# How can metrology support the energy gas transition?

## Need

Ensure the compliance with quality, efficiency, safety requirements

Ensure fair energy gas exchange between countries and trade

## Challenge

Reliability and robustness of measurement results to address the energy transition beyond national boundaries and beyond a single technology

## Solution

European coordinated effort to interface and collect stakeholder needs and to address these needs in the most efficient way at metrological, standardization, and policy level

# European Metrology Network for Energy Gases



# EMN for Energy Gases

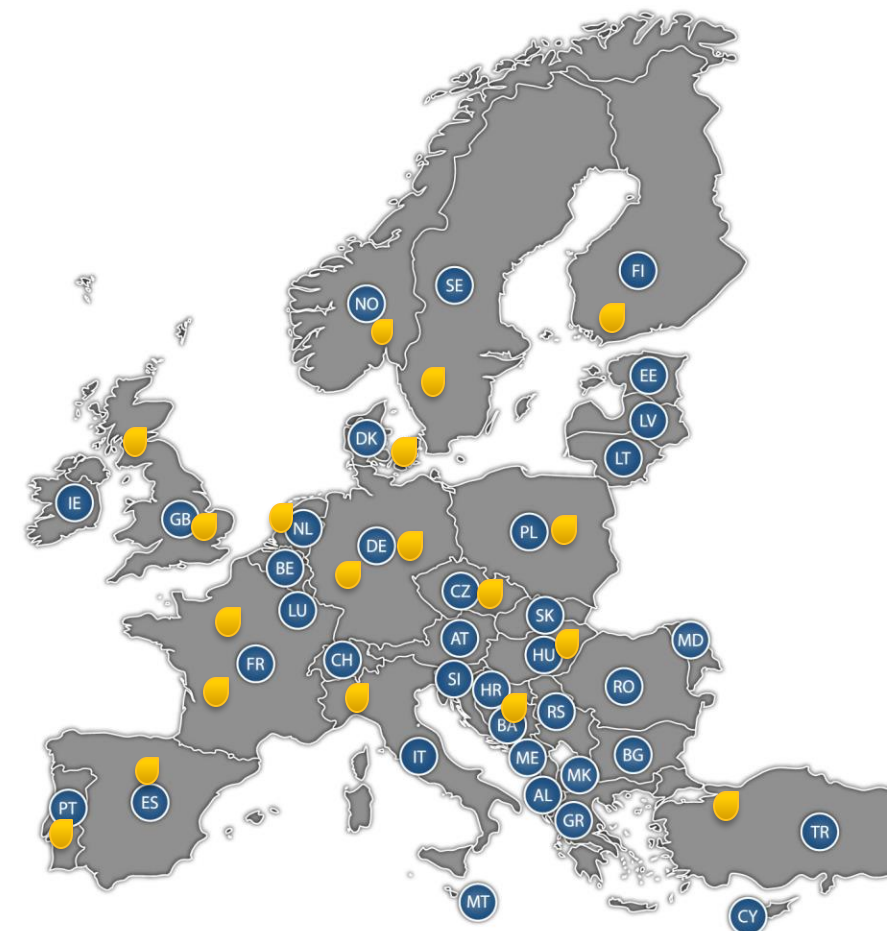


Under EURAMET

Official start: February 2019

19 NMI/DI members

Organisation		Task Groups
Chair:	Annarita Baldan (VSL, NL)	1 – Strategic Research Agenda
Vice-chair	Karine Arrhenius (RISE, SE)	2 – Measurement Service Platform
Secretary	Marcel Workamp (VSL, NL)	3 – Stakeholder Engagement & Standardisation
Steering committee	Henri Foulon (LNE-LADGFR) Heinrich Kipphardt (BAM, DE) Arul Murugan (NPL, UK) Florbela Dias (IPQ, PT) Vito Fericola (INRiM, IT)	4 – General Communication & Impact
		5 – Funding opportunities
		6 - Synergies





# EMN for Energy Gases Fact Sheet



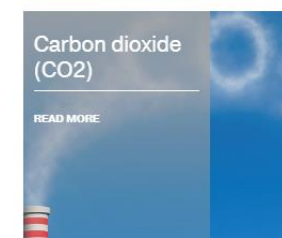
- Focus on **metering and use of energy gases**: conventional fluids and fluids related to (emerging) renewable/ sustainable energy sources, including CCUS
- **Mission**: To provide the world's leading metrology network comprising experts in the field of measurement science to **drive forward innovation** and to **accelerate decarbonisation and emissions reductions** within the energy gas industry in Europe
- ❖ **Engage** with industry, regulation, standardization, policy (e.g. Hydrogen Europe, Clean Hydrogen Partnership, GERG, MARCOGAZ, DG Energy)
- ❖ **Act as European metrology knowledge center** for energy gases ([www.euramet.org/energy-gases](http://www.euramet.org/energy-gases))
- ❖ **Facilitate energy transition** by coordinating measurement research based on stakeholder needs
- ❖ **Boost access** to metrological services and calibration facilities

Cross-cutting character:

<b>Gas composition</b>	<b>Calorimetry</b>
<b>Certified Reference Materials</b>	<b>Particles</b>
<b>Flow</b>	<b>Humidity</b>
<b>Temperature</b>	<b>Material data</b>
<b>Pressure</b>	<b>Material testing</b>

## European Metrology Network for Energy Gases

This network provides measurement science expertise to society and industry to support the implementation of the energy transition to renewable gaseous fuels. Addressing fundamental challenges to establish renewable gases as a fuel source and energy vector is a vital step in striving towards environmental sustainability. By bridging the gap between end-user communities and acting as a central nucleus for measurement science activities, the EMN for Energy Gases will help to establish and facilitate a reliable, safe and diverse energy network.



# EMN Strategic Research Agenda



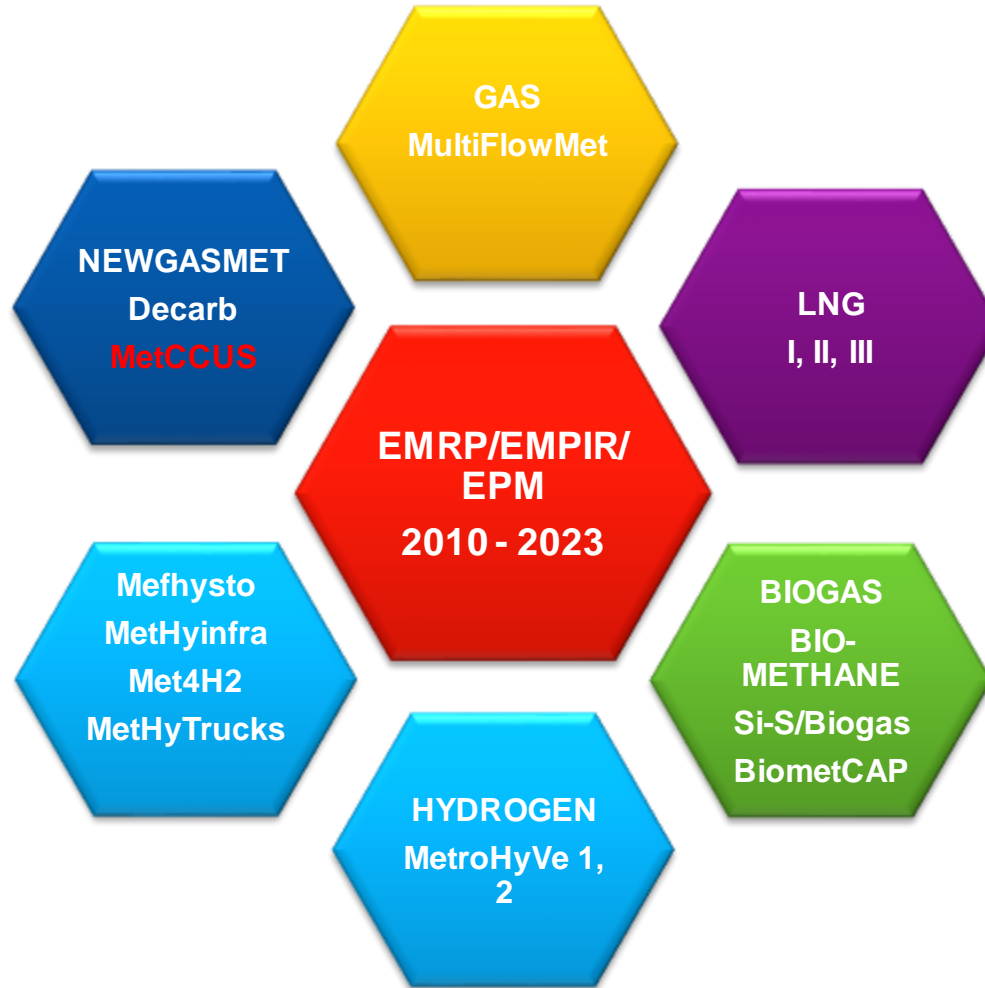
- SRA published on EMN website (2<sup>nd</sup> revision 09/ 2022)
- Focused on measurement needs covering energy gases (natural gas, LNG and LBG, biogas and biomethane and hydrogen) and carbon sequestration and use (CO<sub>2</sub>)
  - **Decarbonising natural gas**
  - **Decarbonising industry**
  - **Energy transport and storage**
  - **Cleaner fuel for mobility**

## Objective:

Facilitate new projects in Research & Innovation and collaboration with industry and other research parties

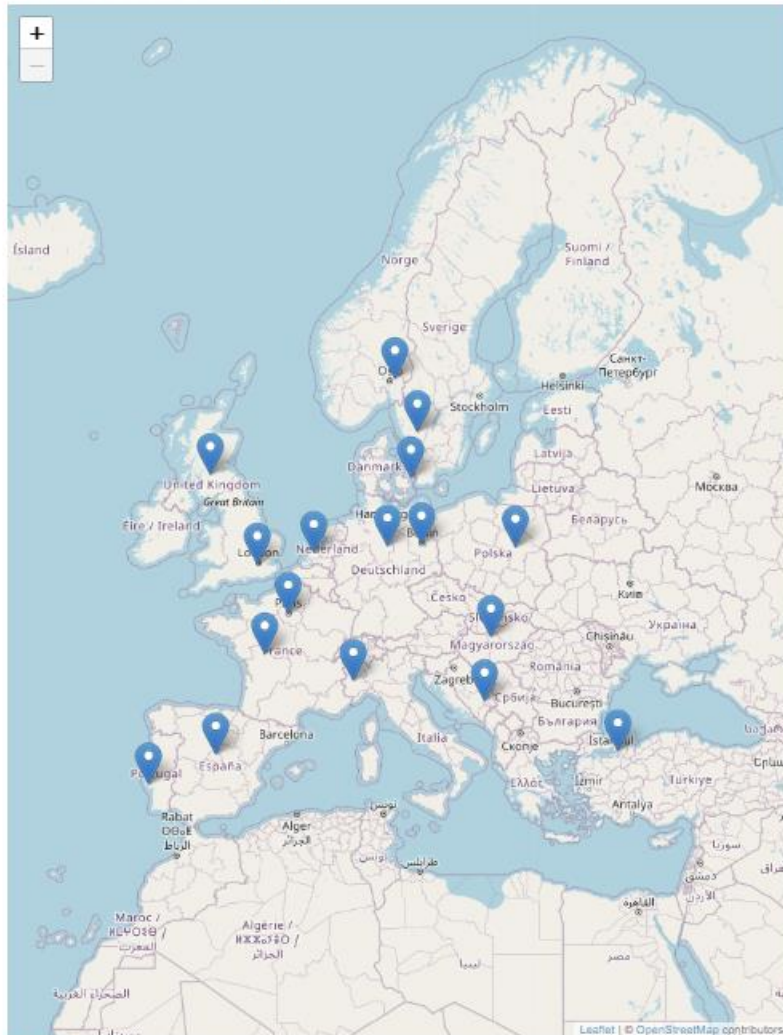


# European Metrological Research in Energy Gases - Portfolio



# Measurement Service Platform

Search for a service



Choose what you want to see on the map:

### Gases

- CO2
- Hydrogen
- H2NG
- Biogas / Biomethane
- LNG/LBG
- Natural Gas

### Services

- Training courses
- Sampling for gas analysis
- Interlaboratory comparisons
- Speed of sound
- Material data
- Material testing
- Calorimetry
- Density (direct)
- Flow
- CRM
- Gas Analysis
- Humidity
- Temperature

17 Ergebnisse

- Overview of the metrological services in Europe
- EMN for Energy Gases website

[www.euramet.org/energy-gases/](http://www.euramet.org/energy-gases/)

### European Metrology Network for Energy Gases

This network provides measurement science expertise to society and industry to support the implementation of the energy transition to renewable gaseous fuels. Addressing fundamental challenges to establish renewable gases as a fuel source and energy vector is a vital step in striving towards environmental sustainability. By bridging the gap between end-user communities and acting as a central nucleus for measurement science activities, the EMN for Energy Gases will help to establish and facilitate a reliable, safe and diverse energy network.



# Conclusions



- Call to action for addressing climate change and energy transition in Europe and worldwide
- European Metrology Network for energy gases established with focus on sustainable energy gases and decarbonization
- Role of Metrology and related research projects to develop measurement methods and standards in support of the energy gas transition
- We look forward engaging with the parties involved in CCUS



Interested in becoming stakeholder ?

More info:

EnergyGases@euramet.org

[www.euramet.org/european-metrology-networks/energy-gases/](http://www.euramet.org/european-metrology-networks/energy-gases/)





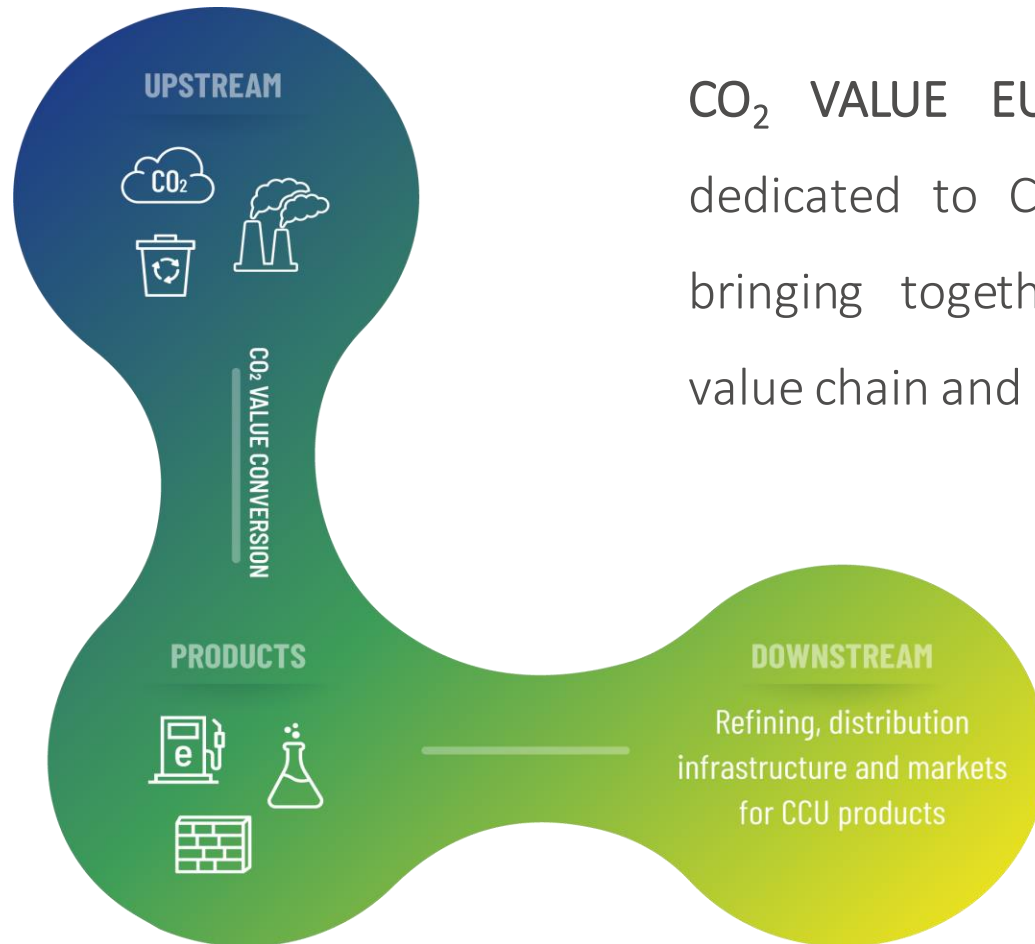
## CCU in Europe – A broad overview

Anastasios Perimenis, Secretary General

MetCCUS

25 October 2023

# The Association



CO<sub>2</sub> VALUE EUROPE is the European association dedicated to Carbon Capture & Utilisation (CCU), bringing together stakeholders from the complete value chain and across industries.



# Membership base (91)



# Priorities

*Provide scientific & technical knowledge and evidence-based information on CCU*

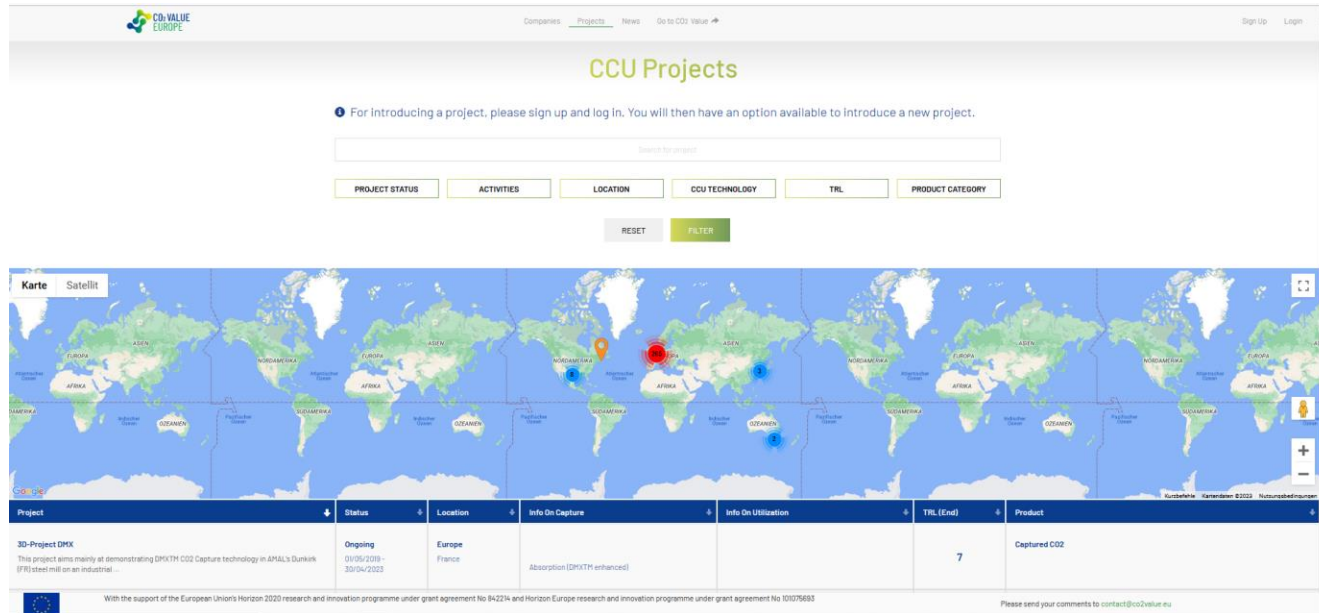
*Raise awareness, engage with stakeholders, communicate about CCU and CVE*



*Create a supportive and consistent regulatory framework for large-scale deployment of CCU*

*Support and accompany the development of both innovative and industrial-scale projects*

# CCU Database



❑ <https://database.co2value.eu/>

❑ Ongoing and upcoming CCU projects

❑ CCU technology providers

❑ News on EU-funded projects

❑ Metrics last 3 months

❑ 1.7 k new users

❑ 2m 21s average engagement time

# Funding

## ❑ Innovation Fund 3<sup>rd</sup> large scale call

❑ 41 projects selected → over €3.6 billion to be granted

❑ 12 projects have a CCU or CCS element

❑ Next: IF23 call (small-, medium-, large-scale call) → 23/11/23 – 09/04/2024 → €4 billion

❑ Next: IF23 auction on renewable hydrogen → 23/11/23 – 08/02/2024 → €800 million

❑ Horizon Europe: more than €235 million granted to R&D&I projects so far



# Policy framework

**NEW** Legislations published in 2023

**SOON** Legislations in the pipeline

<b>NEW</b> REDIII & REDII Delegated Acts	ETS revision	ReFuel EU Aviation	Fuel EU Maritime	Energy Taxation Directive	<b>NEW</b> Carbon Removal Certification	Restoring Sustainable Carbon Cycles
EU Taxonomy for sustainable Finance	Carbon Border Adjustment Mechanism	<b>SOON</b> EU climate targets for 2040	<b>NEW</b> Net Zero Industry Act	<b>SOON</b> Industrial Carbon Management	EU gas & hydrogen package	<b>SOON</b> ETS Delegated Act
<b>SOON</b> Low Carbon Fuels Delegated Act	Sustainable Products Initiative	<b>SOON</b> Delegated Act on cars CO <sub>2</sub> standards	Hydrogen Strategy	Alternative Fuels Infrastructure	<b>NEW</b> Heavy Duty Vehicles Regulation	EU Wind Power Package
Effort Sharing Regulation	<b>NEW</b> Temporary Crisis & Transition Framework	<b>NEW</b> General Block Exemption Regulation	Packaging & Packaging Waste Directive	Energy Efficiency Directive	Climate, Energy, Environmental Aid Guidelines	National Energy Climate Plans
		Recovery and Resilience Facility	Waste Framework Directive	Cross-border renewable energy projects		

# Policy framework

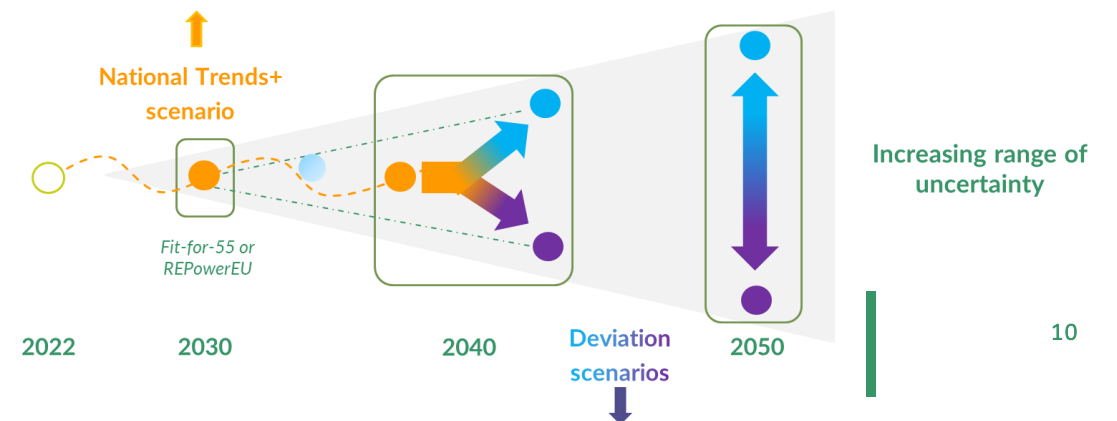
Instrument	Impact on CCU
<a href="#">EU ETS revision</a>	<ul style="list-style-type: none"> <li>✓ CO<sub>2</sub> which is chemically and permanently bound in a product under normal use (e.g. mineralisation) is excluded from the obligation to surrender allowances;</li> <li>✓ Avoid double-counting of emissions released by the use of RFNBOs</li> </ul>
<a href="#">RED revision (REDIII)</a>	<ul style="list-style-type: none"> <li>✓ Combined target of advanced biofuels + RFNBO*: minimum 5.5% of energy in transport by 2030</li> <li>✓ Sub-target for RFNBO: minimum 1% of energy in transport by 2030</li> <li>✓ 42% of the use of hydrogen in the industry to be RFNBOs by 2030, 60% by 2035</li> </ul>
<a href="#">REDII Delegated Acts</a>	<ul style="list-style-type: none"> <li>✓ Rules on additionality, geographical and temporal correlation of RFNBO production</li> <li>✓ Methodology to calculate 70% GHG emission reduction for RFNBO/RCF; eligibility of CO<sub>2</sub> sources (e.g. DAC, bioCO<sub>2</sub>, industrial ETS CO<sub>2</sub> until 2036/2041)</li> </ul>
<a href="#">ReFuelEU Aviation</a>	<ul style="list-style-type: none"> <li>✓ SAFs quotas : min 6%, 20%, 34%, 42%, 70% by 2030/25/40/45/50 respectively</li> <li>✓ Synthetic aviation fuels quotas : min 0.7%** , 5%, 10%, 15%, 35% by 2030/35/40/45/50 respectively</li> </ul>
<a href="#">Fuel EU Maritime</a>	<ul style="list-style-type: none"> <li>✓ Binding GHG reduction targets for ships: 2%, 6%, 14.5%, 31%, 62%, 80% in 2025/30/35/40/45/50, respectively</li> <li>✓ 2% RFNBOs quota in 2034 if RFNBOs account for less than 1% in fuel mix in 2031; multiplier “2”</li> </ul>
<a href="#">Sustainable Carbon Cycles</a> <i>(non legislative)</i>	<ul style="list-style-type: none"> <li>✓ Min. 20% of carbon in chemical and plastic products should be from sustainable non-fossil sources by 2030</li> <li>✓ Tracing the origin of CO<sub>2</sub> used in products</li> </ul>
<a href="#">Energy Taxation revision (on-going)</a>	<ul style="list-style-type: none"> <li>✓ Minimum taxation rate of zero for 10 years for RFNBOs for specific types of air and waterborne navigation.</li> </ul>
<a href="#">Net Zero Industry Act (new)</a>	<ul style="list-style-type: none"> <li>✓ CCU is a net-zero technology, but not a “strategic” net-zero technology</li> </ul>
<a href="#">EU Certification for Carbon Removals</a>	<ul style="list-style-type: none"> <li>✓ DAC/BioCO<sub>2</sub> to mineralisation recognised as removal</li> </ul>

# CCUS Forum & the Industrial Carbon Management Strategy

- ❑ Stakeholder Platform providing inputs for the elaboration of the ICMS (CCS, CCU, CDR)
- ❑ Working Groups on Industrial Partnership, Infrastructure, Public perception, Strategy elaboration
  - ❑ *Infrastructure focus:*
    - ❑ *Issue paper: [Towards a European cross-border CO<sub>2</sub> transport and storage infrastructure](#)*
    - ❑ *Issue paper: [An interoperable CO<sub>2</sub> transport network – towards specifications for the transport of impure CO<sub>2</sub>](#)*
    - ❑ *Study: [EU regulation for the development of the market for CO<sub>2</sub> transport and storage](#)*
    - ❑ *Study under preparation by JRC on scenarios of infrastructure development for cross-border CO<sub>2</sub> transport*
- ❑ CCUS Forum plenary 27-28/11 in Aalborg
- ❑ ICMS to be published during Q1 2024

# Ten Year Network Development Plan (TYNDP)

- ❑ Bi-annual exercise for the develop of scenarios for the future energy system conducted by ENTSO-E and ENTSO-G
- ❑ Building from national investment plans prepared by TSOs & stakeholder feedback on parameters and methodologies, the TYNDP models scenarios of future infrastructure development.
- ❑ CVE is part of the External Technical Advisory Group as CCU/CCS stakeholders have been expressly requested
- ❑ To be seen how CO<sub>2</sub> transport will be integrated in the TYNDP
- ❑ [Webinar](#) on future system needs on 06/11

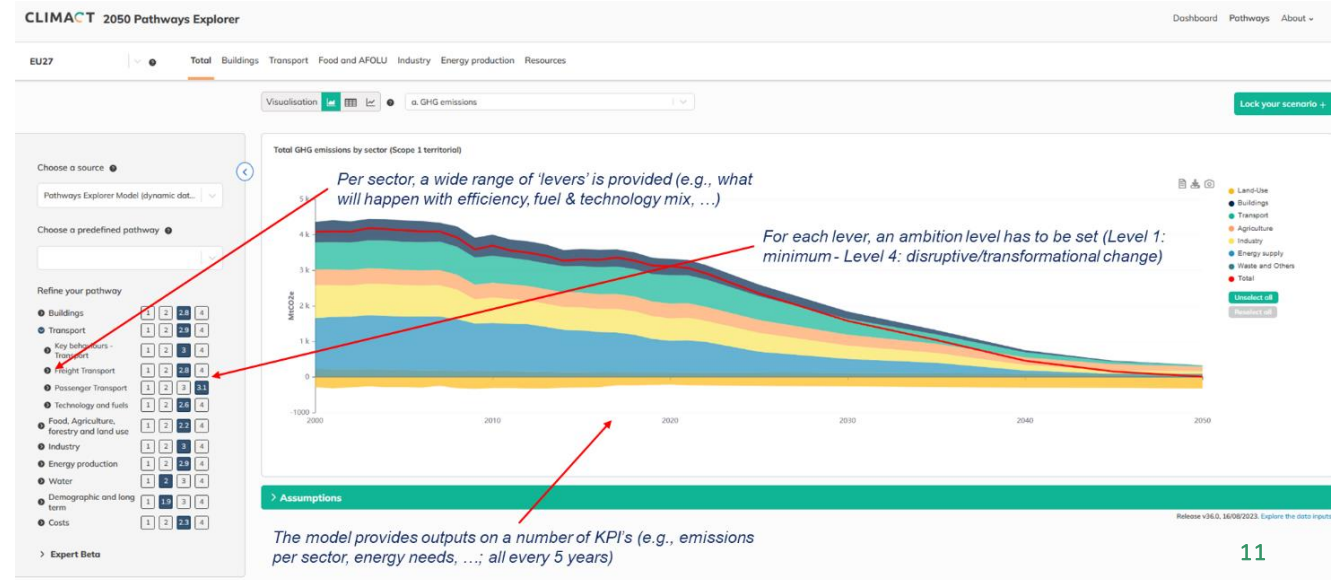




# CCU's contribution to net-zero

## CVE's EU Roadmap for CCU deployment by 2050

- ❑ Scenario development and modeling of CCU pathways
- ❑ How much can CCU contribute towards EU's climate neutrality goals ?
- ❑ How much carbon do we need to capture ?
- ❑ How much captured carbon can be converted to fuels, chemicals and materials ?
- ❑ How much electricity will we need ?
- ❑ Available as of mid-November





# Thank you!

[anastasios.perimenis@co2value.eu](mailto:anastasios.perimenis@co2value.eu)

[www.co2value.eu](http://www.co2value.eu)

***FOLLOW US ON***



**in**



› **REQUIREMENTS FOR CO<sub>2</sub> FLOW MEASUREMENT ACCURACY**  
**FILIP NEELE**

METCCUS – OCTOBER 26, 2023

# › CCS DEVELOPMENTS IN EUROPE FROM SIMPLE TO COMPLEX

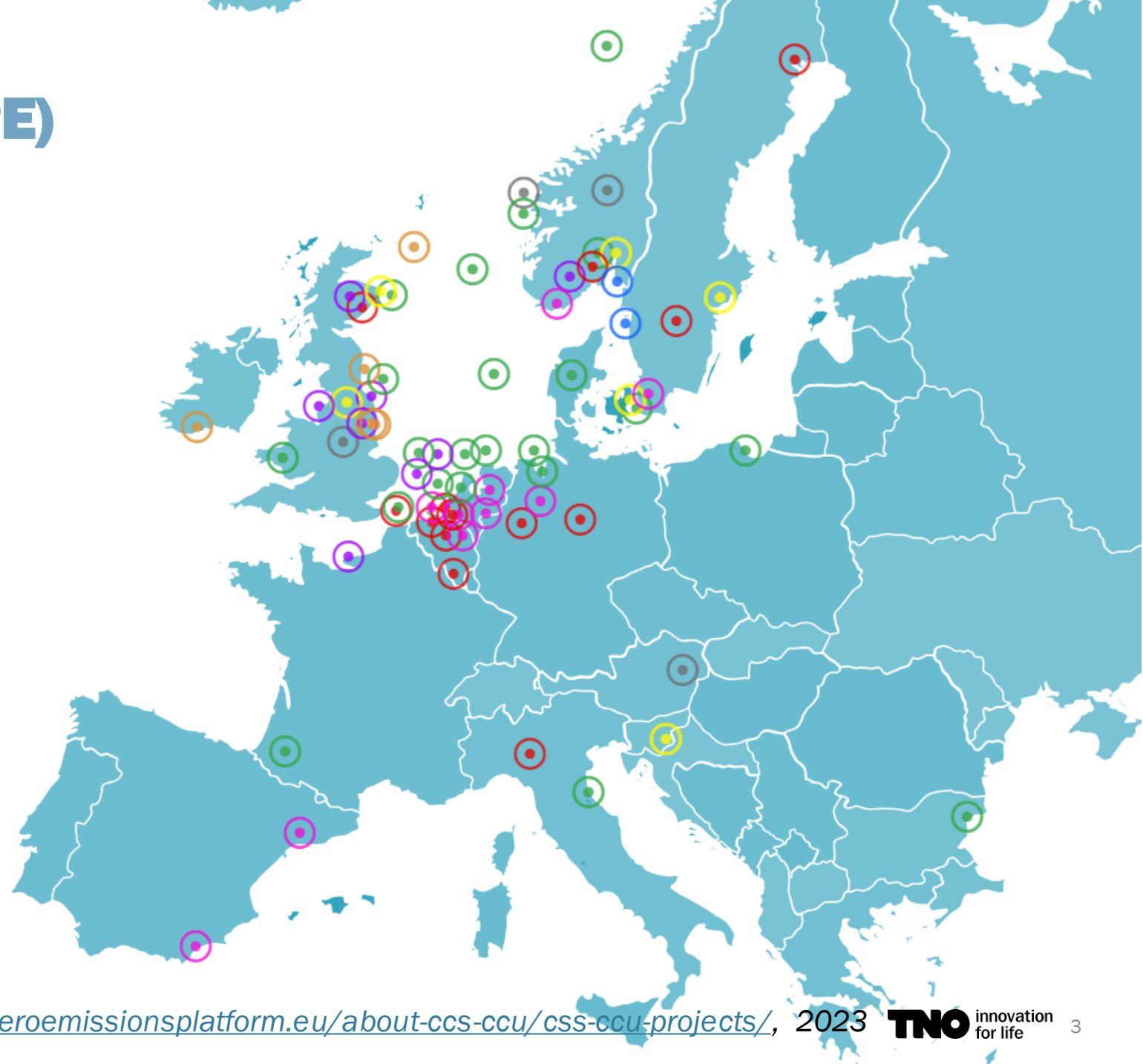
1. CCS developments switching to higher gear
  - › Many new projects in recent years
  - › No commercial CCS transport & storage projects in operation yet
2. Focus on NL
  - › Several projects in development
  - › Complex CCS infrastructure expected
3. Transport modalities
  - › First projects: pipeline, ship
  - › More modalities to follow soon



# › CCS PROJECTS (EUROPE)

- › Project count (mid 2023): >60
- › Several storage projects to come online in period 2025 – 2030
  - › Linking onshore emitters to offshore storage capacity

- Full-chain CCS – 4 (Orange)
- CO2 transport and storage – 19 (Green)
- CCS in industry – 12 (Red)
- CCS in energy production – 7 (Yellow)
- Low-carbon hydrogen production – 8 (Purple)
- Carbon Capture and Utilisation – 9 (Pink)
- Test centre – 4 (Grey)
- Limited information available (3) (Blue)



## › CCS PROJECTS (EUROPE)

- › 65 CCS projects in Europe in development
- › Several modes of transport
  - › Pipeline, ship, barge
  - › Train, truck
- › Many interfaces

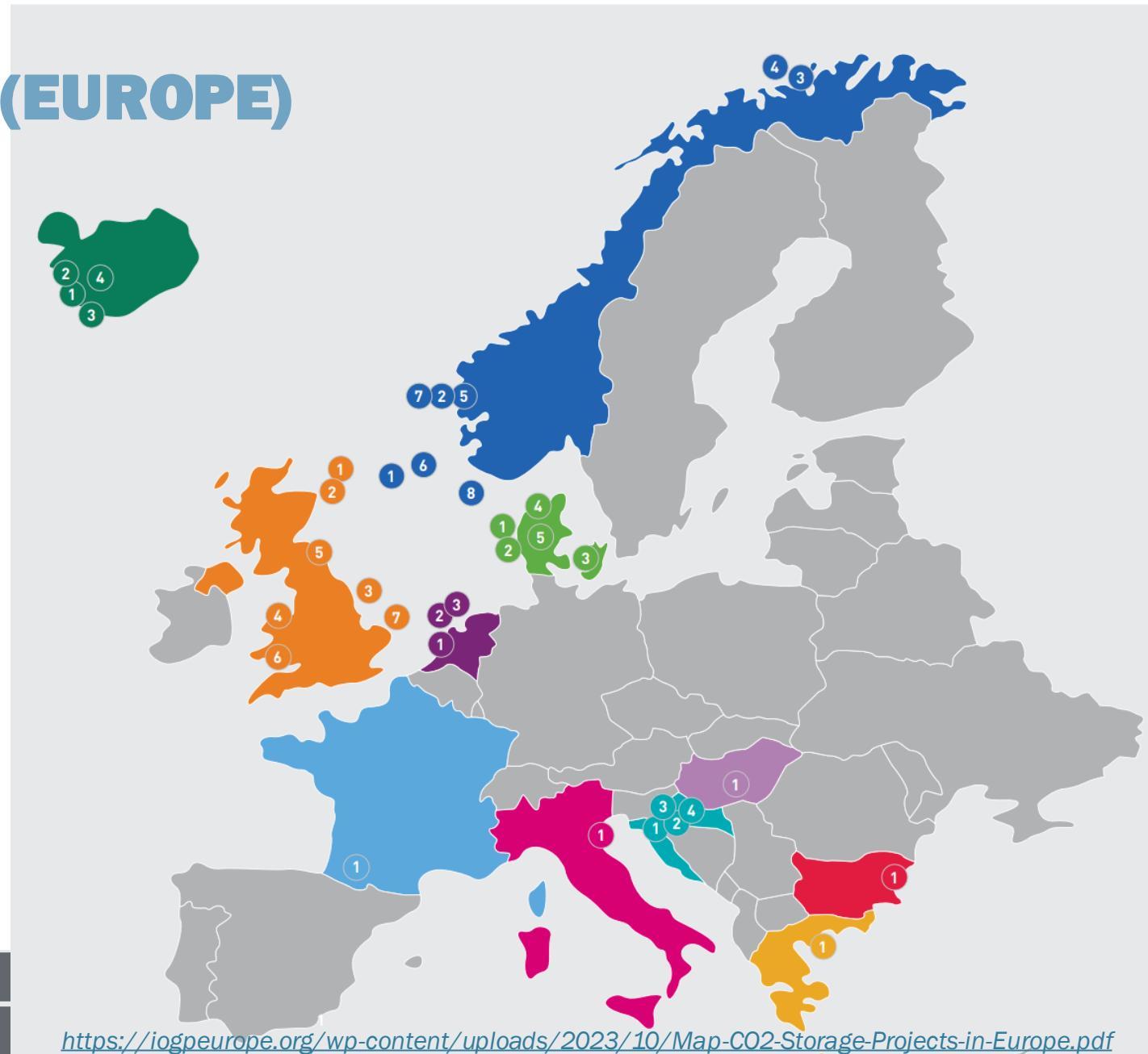
Total number of projects: **65**  
Around 60 MtCO<sub>2</sub>/yr stored by 2030



## › CO<sub>2</sub> STORAGE PROJECTS (EUROPE)

- › Many CCS projects around the North Sea
- › Many storage projects close to financial investment decision; many projects in feasibility phase
- › Transport to these projects
  - › Pipeline (gas phase)
  - › Pipeline (dense phase)
  - › Pipeline gas *and* dense phase
  - › Ship (medium pressure)
  - › Ship (low pressure)

EU	17 projects - 35 MtCO <sub>2</sub> /yr by 2030
Europe	36 projects - 110 MtCO <sub>2</sub> /yr by 2030



# CO<sub>2</sub> TRANSPORT AND STORAGE

## CURRENT PROJECTS: PCI/PMI CANDIDATES

› First elements of pan-European transport infrastructure

› Offshore:

› Pipeline

› Ship to port

› Ship to well

› Onshore:

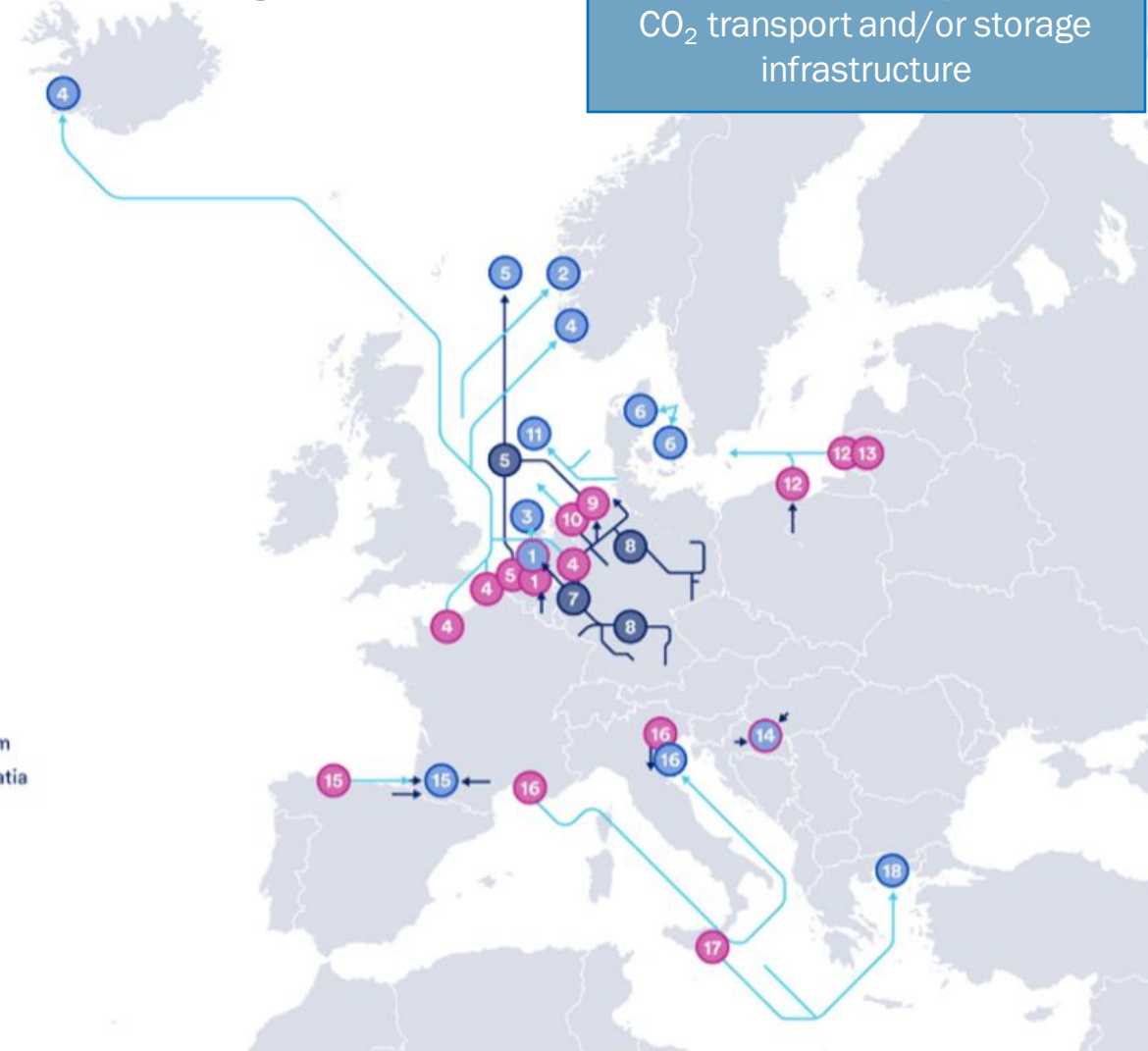
› Train, barge

› Truck being considered

### Carbon Capture, Removal, Transport and Storage in Europe



- |                                 |                                    |
|---------------------------------|------------------------------------|
| 1. CO <sub>2</sub> TransPorts   | 10. Noordkaap                      |
| 2. N-LITES                      | 11. Bifrost                        |
| 3. Aramis                       | 12. ECO <sub>2</sub> CEE           |
| 4. Nautilus                     | 13. CCS Baltic Consortium          |
| 5. EU2NSEA                      | 14. Geothermal CCS Croatia         |
| 6. Norne                        | 15. Pycasso                        |
| 7. Delta Rhyne Corridor         | 16. Callisto                       |
| 8. German Carbon Transport Grid | 17. Augusta C <sub>2</sub>         |
| 9. WH2V (eNG Hub phase 1)       | 18. Prinos CO <sub>2</sub> Storage |



PCI: Project of Common Interest  
PMI: Project of Mutual Interest

Projects with PCI and PMI status can access EU funding to develop CO<sub>2</sub> transport and/or storage infrastructure



# CO<sub>2</sub> TRANSPORT AND STORAGE IN NL

## SIMPLE FIRST, COMPLEX LATER?

- › Porthos project (*FID taken Oct 2023*)
  - › P18 gas field cluster (~40 Mt, 2.5 Mtpa)
- › Aramis project
  - › Trunkline Rotterdam – K,L blocks: 22 Mtpa (!)
  - › Shell: K14-FA (47 Mt, 2.5 Mtpa)
  - › TotalEnergies: L4-A, K6-CA (40 Mt, 2.5 Mtpa)
- › CO2Next collection hub + ship terminal Rotterdam
- › Neptune Energy
  - › L10 fields (120-150 Mt, 5 Mtpa)
- › WintershalIDEA CMS
  - › Q1B, P6 (~60-70 Mt, ? Mtpa)
- › All expected to start in period 2026 - 2030



Aramis



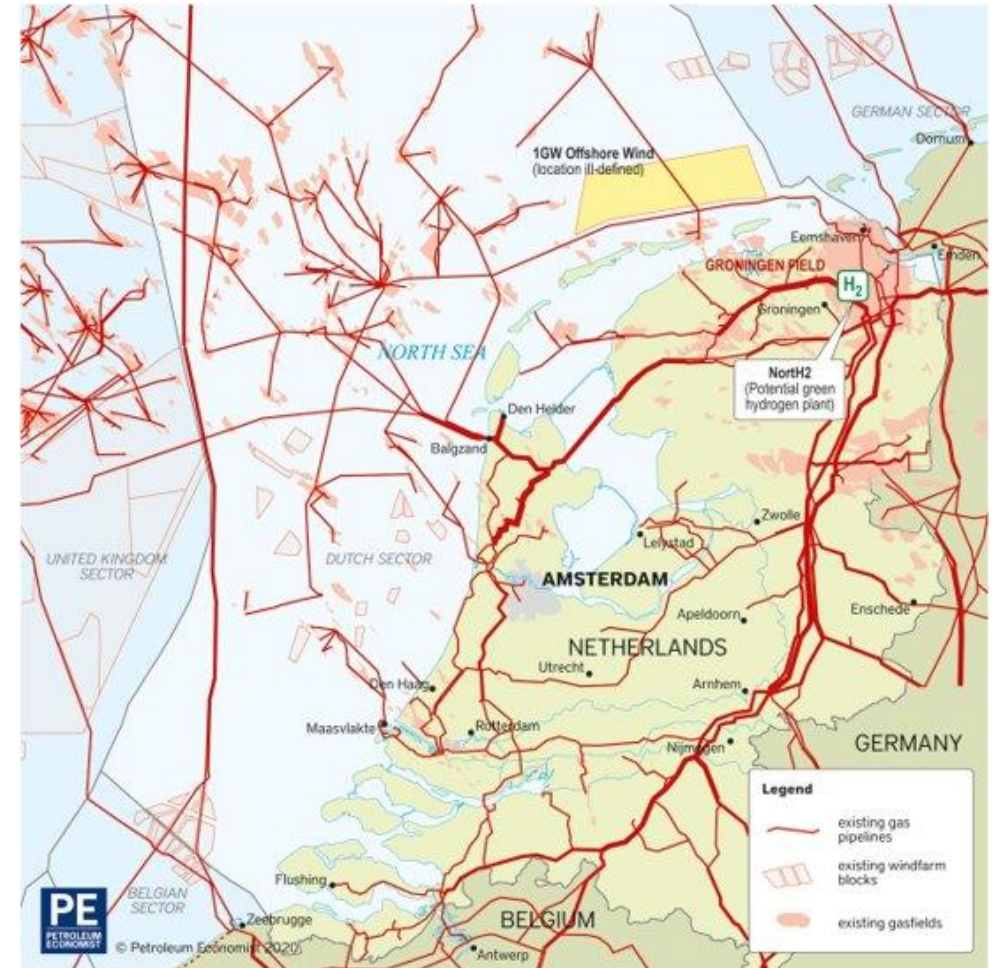
Porthos



Neptune Energy

# › NETHERLANDS: FOCUS ON DEPLETED FIELDS TOWARDS COMPLEX NETWORKS

- › ~100 fields, ~1700 Mt capacity (EBN-Gasunie, 2017)
- › Domestic capture rates could go to **dozens of Mtpa**
- › Neighbouring countries Belgium, Germany, France
  - › Little or no domestic storage capacity
  - › Likely to connect to Netherlands offshore
  - › Volume also **dozens of Mtpa** (post-2035)
- › Storage in NL fields: at capacity by ~2060
  - › Connections needed with UK, DK, NO networks and stores
- › Metering needed at *many* interfaces along CCS chains

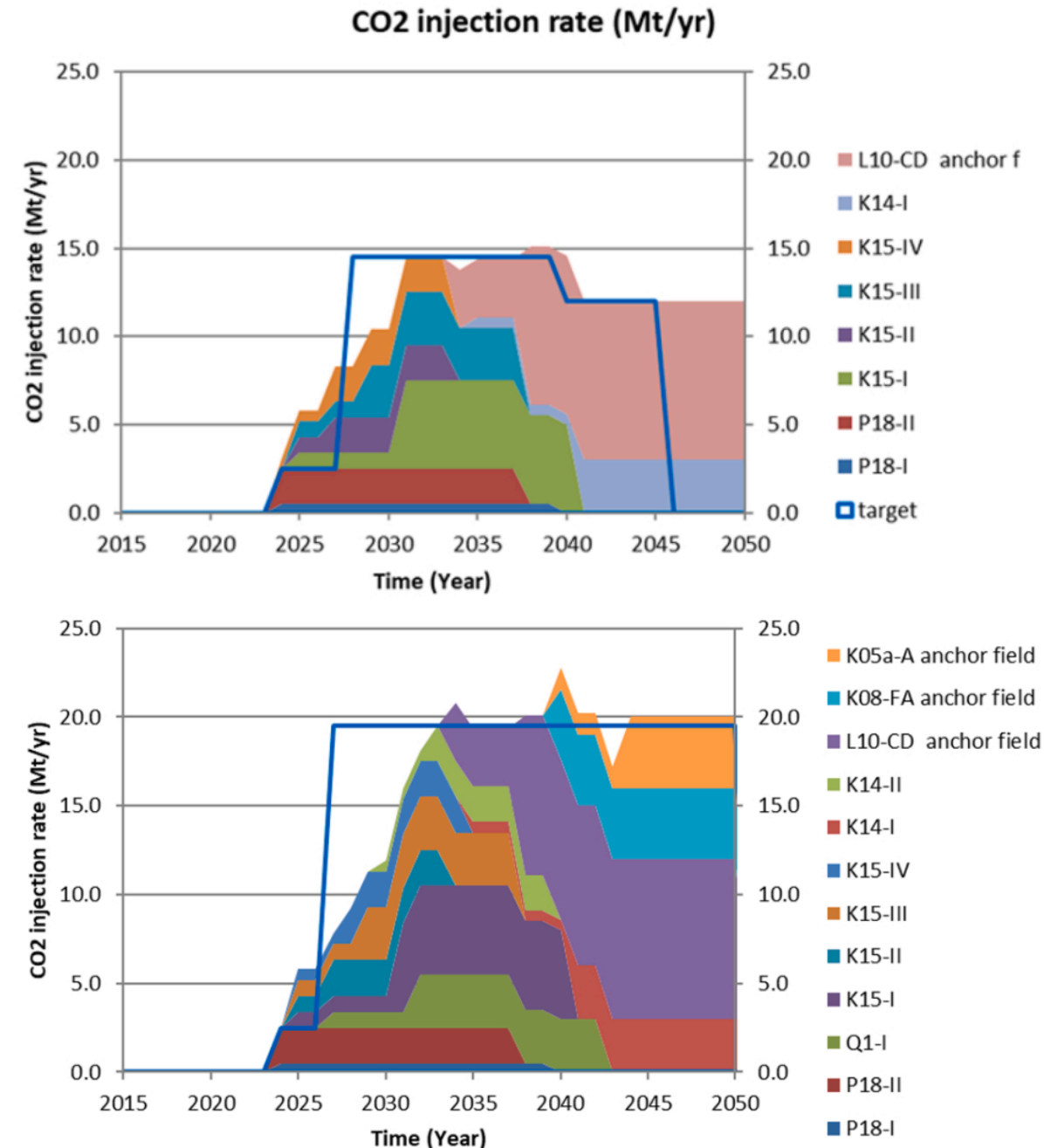


Current gas pipelines and gas fields

# › FOCUS ON DEPLETED FIELDS

## STACKING OF FIELDS

- › NL offshore: many gas fields
  - › Storage capacity 10-50 Mt (typically)
  - › Fields to be operated in parallel to reach significant rates
- › Examples of supply scenarios
  - › ‘Stacking’ of fields
  - › Need several / many fields simultaneously
- › Variability in CO<sub>2</sub> streams
  - › Composition
  - › Uptime, downtime of suppliers and network elements
- › Flow rate uncertainty ~1%
  - › *Much* larger than potential (geological) leakage...



# › CCS DEVELOPMENT METERING ASPECTS

- › Transport and storage system elements
  - › Pipelines, ships, buffers, train, truck
- › CO<sub>2</sub> conditions
  - › Gas phase (collection networks)
  - › Liquid phase (buffer, ship)
  - › Dense phase (high-p pipelines)
- › CO<sub>2</sub> composition
  - › Variable, 95 – 99% purity

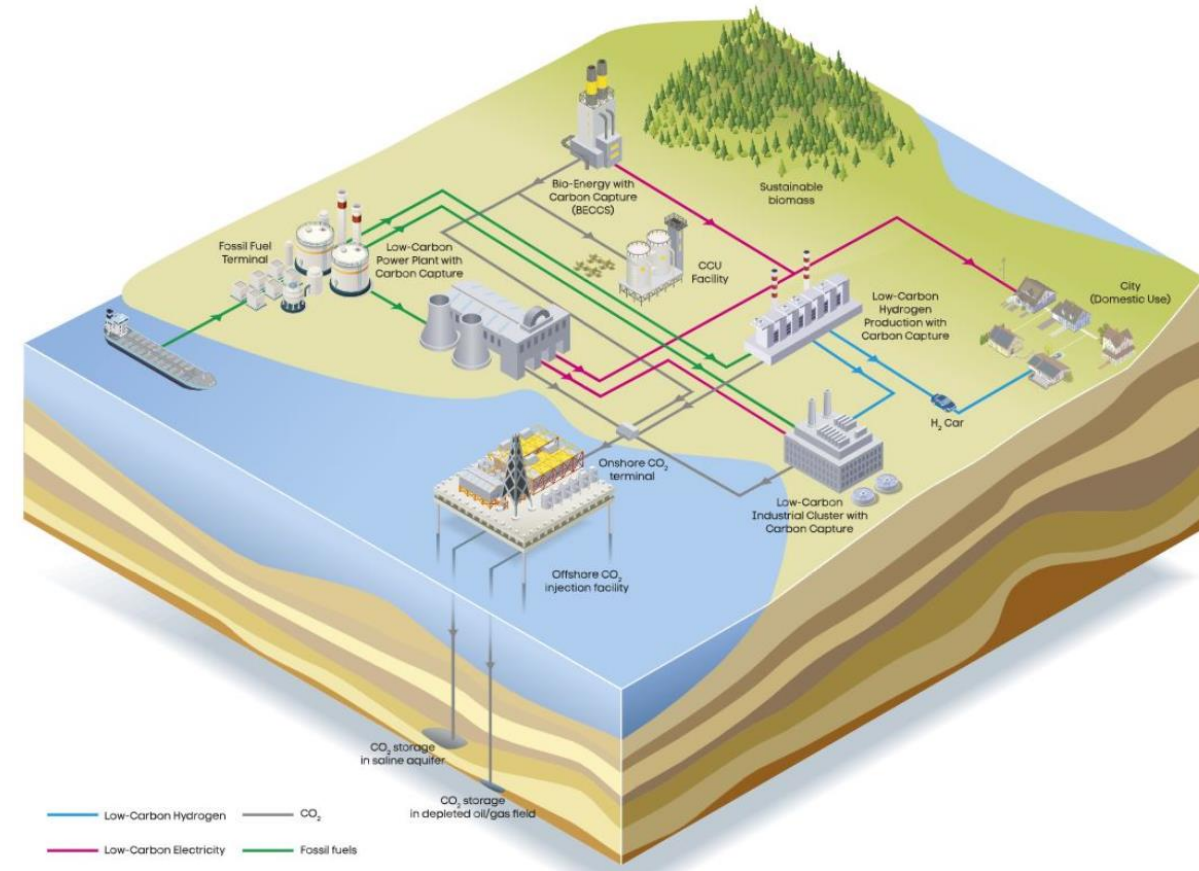


## Requirements for flow measurements

- › CCS Directive (permitting storage)
  - › Flow into each well
- › Storage operator (contracts with emitters)
  - › Flow to storage site (= one or more wells)
- › Ship terminal (buffering flow into pipeline)
  - › Inflow, outflow
- › Hub / node in network (distributing flow)
  - › Flow to hub, flow to each branch

# › CCS DEVELOPMENTS WRAP UP

- › CO<sub>2</sub> transport and storage
  - › Rapidly growing interest, projects are developing
- › Transport modalities
  - › Pipeline, ship, train (, truck)
- › CO<sub>2</sub> specifications
  - › Variable, purity 95% and higher
- › There is a clear need for metering of:
  - › CO<sub>2</sub> flows with CO<sub>2</sub> in gas, liquid, dense phase
  - › CO<sub>2</sub> with variable purity
  - › Flow rates in range of up to 20 Mtpa





› **THANK YOU FOR  
YOUR TIME**

**TNO** innovation  
for life

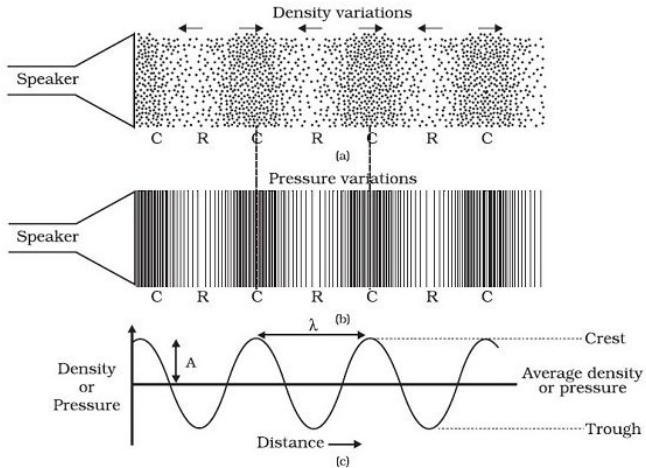
Metrology support for Carbon Capture Utilization and Storage  
26<sup>th</sup> October 2023

## Seminar on Metrology Support for Carbon Capture, Utilisation and Storage

# Exploitation of speed of sound measurements for monitoring CCUS processes

P. Alberto Giuliano Albo (INRiM)  
(a.albo@inrim.it)

# Ultrasonic propagation



Acoustic waves are a phenomenon of **transportation of mechanical energy** through an **elastic medium** (solid, liquid, gas, supercritical, ...)

Acoustic waves are used to **perturb the thermodynamic system** and setting it out of its equilibrium. **Monitoring** how the system backs to its equilibrium, it is possible to **characterize some properties** of a physical system;

Speed of sound is a **thermodynamic property** useful to implement high accurate **equations of state of a fluid**.

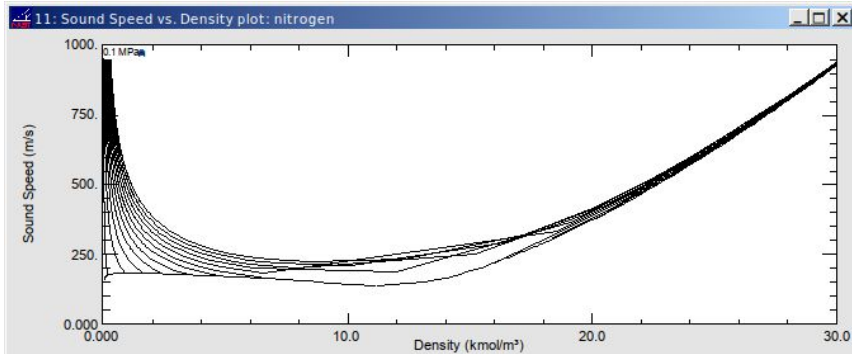
Ultrasonic waves are widely used in industrial for **non-invasive measurements** and **non-destructive-testing (NDT)**;

Acoustic wave are used to **create pseudo-images** including **quantitative information** (elastic properties, acoustic impedance, ecc);





# CO<sub>2</sub> phase identification



## References:

Two freq.: <https://doi.org/10.1016/j.measen.2021.100040>

VLE/VLLE: [https://doi.org/10.1016/S0378-3812\(00\)00380-0](https://doi.org/10.1016/S0378-3812(00)00380-0)

Fluid phase can be monitored by measuring temperature and pressure when the **composition** is known, however when it is not known with the necessary accuracy, **two low-cost transducers** can be adopted:

- one at low-frequency ~250 kHz;
- one at ~5 MHz (or more for pressure higher than 6 MPa).

**High frequency** ultrasonic waves are **absorbed** by gases and they do not propagate (usually below 6 MPa for 5 MHz signals).

**Noisy signals** at 5 MHz in liquids indicate presence of bubbles and the presence **multiphase-fluid**.

In **supercritical fluids** very high **frequency signals** can be **absorbed**.

# Ultrasonic flow meters calibration

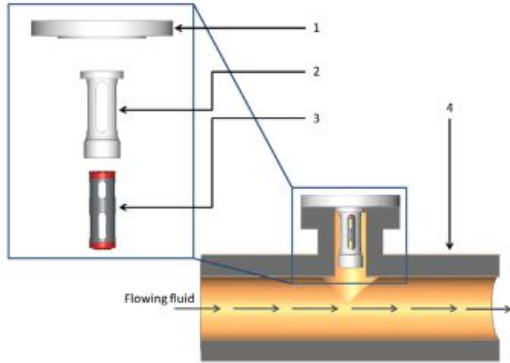


Fig. 8. Scheme which shows how the ultrasonic cell can be used as a transfer standard by mounting it directly on the pipelines where LNGs flow, in vicinity of the ultrasonic flowmeters to be calibrated. (1) DN 50 flange; (2) Stainless steel support for the ultrasonic cell; (3) Ultrasonic cell; (4) LNG pipeline T-connection.

## On-line 2<sup>nd</sup> calibration:

We are checking the possibility to use a **primary standard** to transfer the measurement of **speed of sound** from laboratory to installed ultrasonic flowmeters, exploiting the possibility of meters to determine the speed of sound of the fluid at rest.

## Calibration check:

We are developing a **clamp-on system**:

- able to operate both in **gas and in liquid**;
- **fully traceable** (but with a higher uncertainty in the begin);
- equipped with **laboratory instrumentation**, suitable to work in field, for waveform analysis;

## References:

<https://doi.org/10.1016/j.measurement.2021.109526>

# IoT and Equations of state



IoT technology can **support** the development of low cost **metrological measurement networks**, easily adaptable for specific scopes (flow metering, leak detection, tanks and reservoir monitoring, ecc).

IoT allows to **integrate established** instrumentation with **new technologies**.

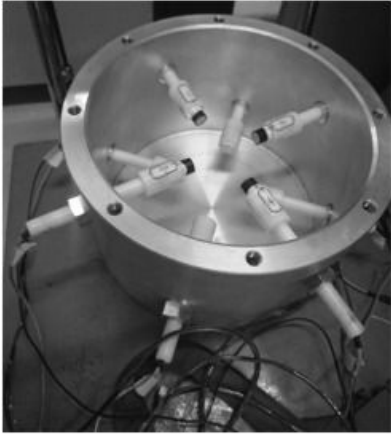
Equations of state are **the core of flow-computers** used to account for transferred fluids.

- They **convert** volume to mass flow, knowing the composition;
- They can be used **design** chemical and measurement processes;
- They can be used to **check** the instrumentation, when composition is known;
- Using some **particular fluid**, equation of state can be used to **calibrate instrumentation**;

**GERG-2008** is a **standard equation of state** that proved to be consistent with the best experimental measurements from cryogenic to high temperature. However it has some limitations (fluid matrix and compositions)

**Updating new equations** including amines and  $\text{CO}_2$

# Impurities



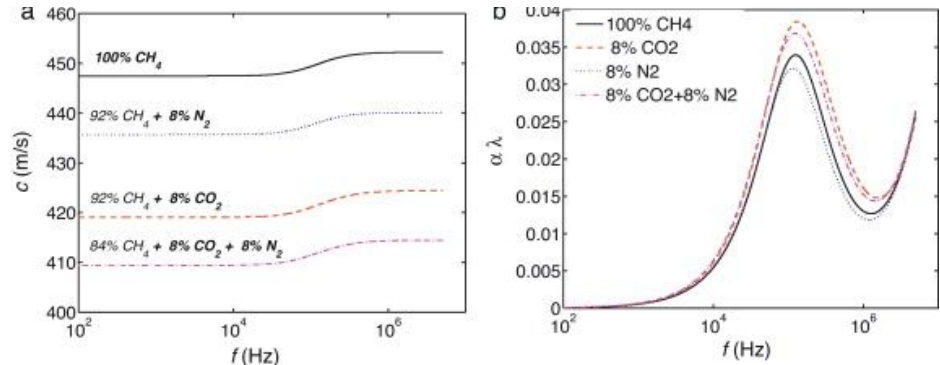
**Quantitative Acoustic Relaxation Spectroscopy (QARS)** can be used to monitor the content of  $\text{CO}_2$ , in presence of impurities, by using **transducers** working at **two different frequencies**. At the moment the error is in the order of 1 % but it is a **promising, fast, and cheap** solution.

**Main impurities:** Amine,  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{NO}_x$ ,  $\text{SO}_x$ , CO,  $\text{H}_2\text{S}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2^+$ ,  $\text{NH}_3$

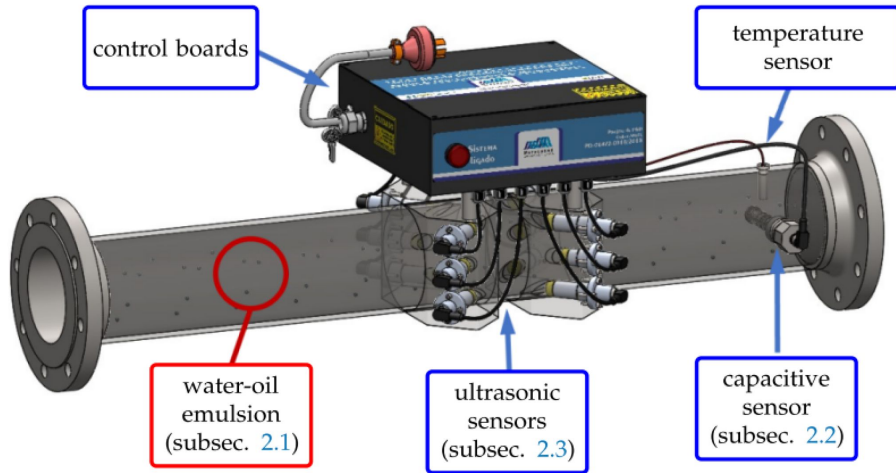
Effects on **speed of sound** can be **predicted** using Gerg 2008 with few exceptions.

## Reference:

- <https://doi.org/10.1016/j.measen.2021.100040>
- <https://doi.org/10.1016/j.snb.2012.03.086>
- <https://blog.sintef.com/sintefenergy/energy-efficiency/what-else-is-there-in-co2-except-co2/>



# Monitoring Methanation and e-fuels production



Combined ultrasonic and capacitive sensors are under development and characterization for obtaining quantitative information on the quality of the produced oil or fuel.

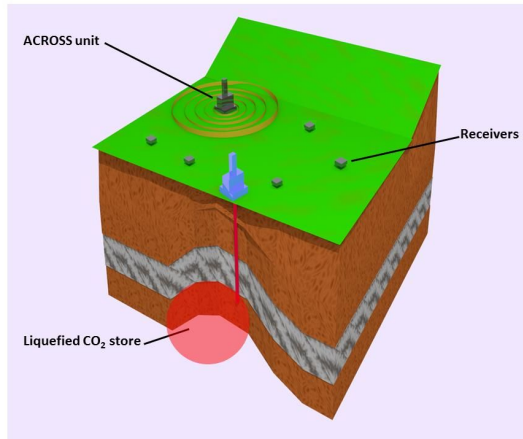
At the moment, **density** is **estimated** with an uncertainty better than **1%** but significant improvements are expected since research just started.

The idea of combining **dielectric constant** and **speed of sound** seems promising. If not those quantities, some other might be more useful.

## Reference:

- <https://www.mdpi.com/1424-8220/21/23/7979#>
- <https://doi.org/10.5194/jsss-2-103-2013>

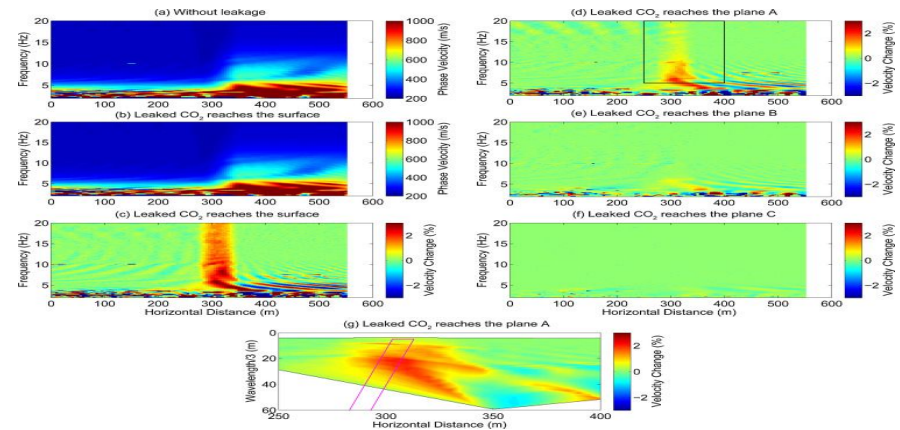
# CO<sub>2</sub> storage: site monitor



An example of **monitoring** system based on subsonic wave propagation is called Accurately Controlled Routinely Operated Signal System (ACROSS).

Frequencies between (5 and 15) Hz.

Variation of **speed of sound** in rocks is used to monitor CO<sub>2</sub> **leakage** from the storage site.

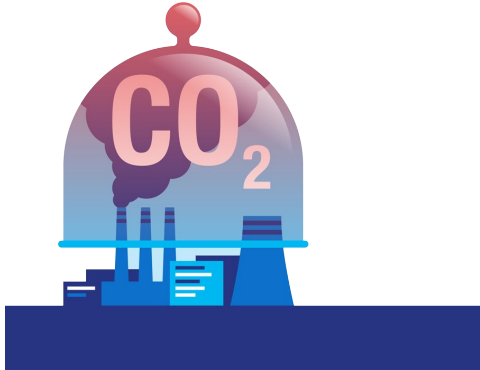


## References:

- <https://doi.org/10.1016/j.ijggc.2012.07.026>
- <https://doi.org/10.3390/en16010012>
- <https://doi.org/10.1016/j.ijggc.2015.11.030>



# Conclusions



- **Applications** of ultrasonic and subsonic waves in different fields of CO<sub>2</sub> processing;
- **New and established technologies** based on mechanical wave propagation;
- New technologies can provide necessary information on CO<sub>2</sub> systems and **reduce costs**;
- **Research** to support of the energy transition needs to **be directed by industry** to be of real impact. A tight collaboration would be useful for both;
- **Keep in touch! Stay tuned with [MetCCUS](#)** activities and participants;

# Capabilities and Opportunities

---

Salvatore Pitti  
Application Engineer Custody Transfer / Meter Performance  
Emerson – Metrology Department





# Agenda

- Scope
- Approval stage
  - Regulations – Standards and Legislations
  - JIPs and advisory boards
- Applications and Measurements in CCUS
- Prove of transferability
- Summary

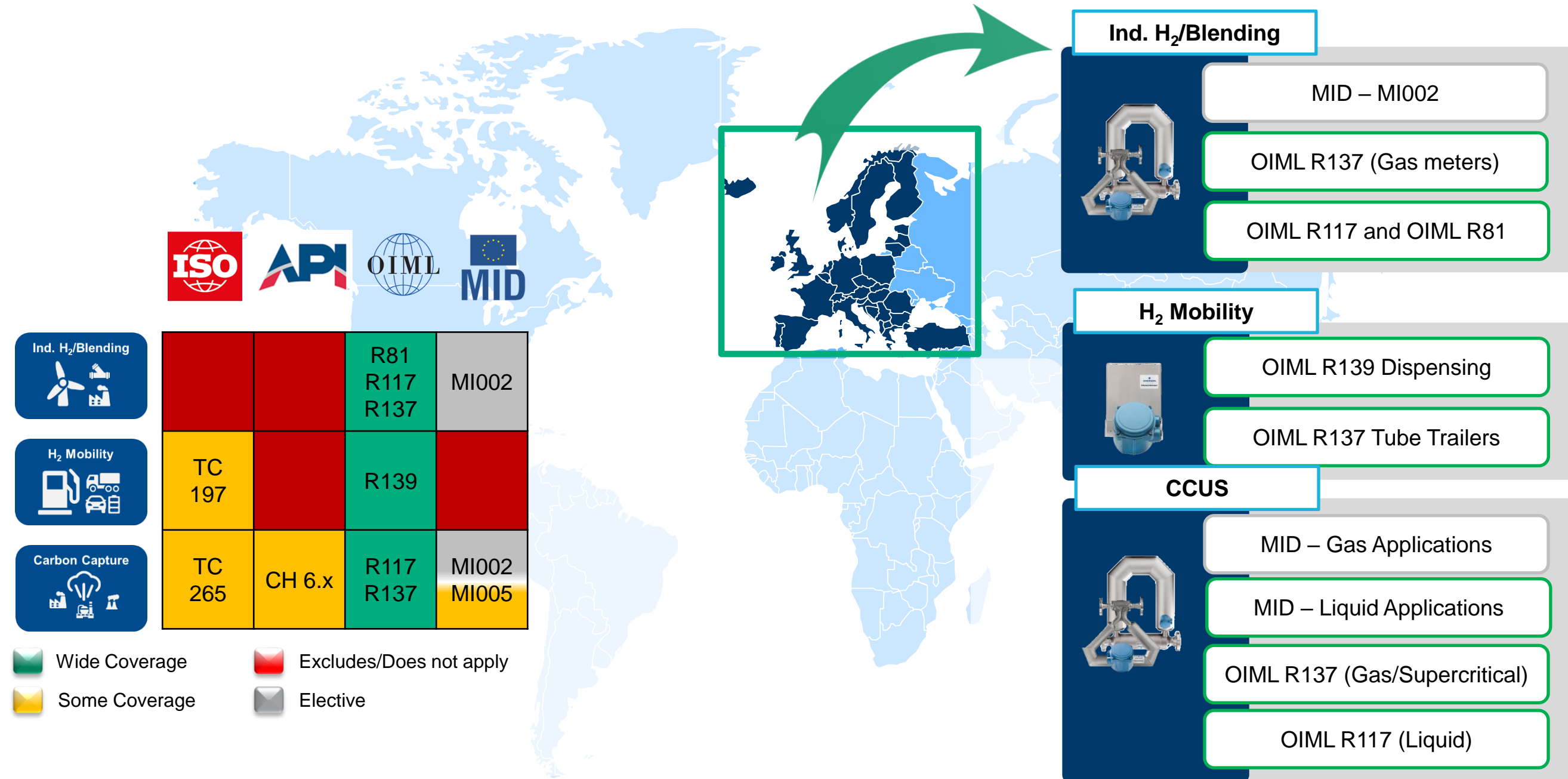
## Scope

- For conventional measurement, like oil and gas, regulations are decennia in place. Locally, Regional dependent and even up to a level of harmonization (think of OIML or MID).
- For H<sub>2</sub> and for CO<sub>2</sub> regulations are in development and in the strength and speed of the world we are all aware for good accommodation of this necessity.
- What are the capabilities in measurement per today, and what are the capabilities of regulations in the world per today and do we have challenges forward are all questions we would like an answer on.

# Approval stage

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# Standards and Legislations for H<sub>2</sub> and CCUS Economy



# Standards and Legislations for H<sub>2</sub> and CCUS Economy

## H<sub>2</sub>

### Relevant Regulations/Recommendations on H<sub>2</sub> Measurement:

- OIML R137 2012, Gas meters, Section 5.3.2, **Accuracy class 0.5, 1 and 1.5.**
- OIML R139 2018R, Hydrogen Dispensing Section 5.2.1, **Accuracy Class 1.5, 2 and 4 for the system and Accuracy Class 1, 1.5 and 2 for the Meter respectively**

## CCUS

### Relevant Regulations/Recommendations on CO<sub>2</sub> Measurement:

- EU, 8 June 2010 amending Decision 2007/589/EC, Section 5.7 Transferred CO<sub>2</sub>: The mass of annually transferred CO<sub>2</sub> or carbonate shall be determined with a **maximum uncertainty of less than 1,5%** either directly by using volume or mass flow meters.
- ETS M&R Regulation 2018/2066, Annex VIII CO<sub>2</sub> transfer Tier 4: In case of CO<sub>2</sub>, the uncertainty is to be applied to the **total amount of CO<sub>2</sub> measured ± 2.5%**
- EU MID (Directive 2014/32) Liquefied CO<sub>2</sub>, Annex VII Accuracy class 1.5: **Measuring Systems ± 1.5% and Meters ± 1%**
- OIML R 117 2007E, Liquefied CO<sub>2</sub> Section 2 Accuracy class 1.5: **Measuring Systems ± 1.5% and Meters ± 1%**
- NIST Handbook 44-2017, Liquid CO<sub>2</sub> Measuring Devices Section 3.38 Accuracy class 2.5: **Acceptance Tolerance ± 1.5% and Maintenance Tolerance ± 2.5%**
- OIML R137 2012, Gas meters, Section 5.3.2, **Accuracy class 0.5, 1 and 1.5.**

# Leading with Technical Expertise

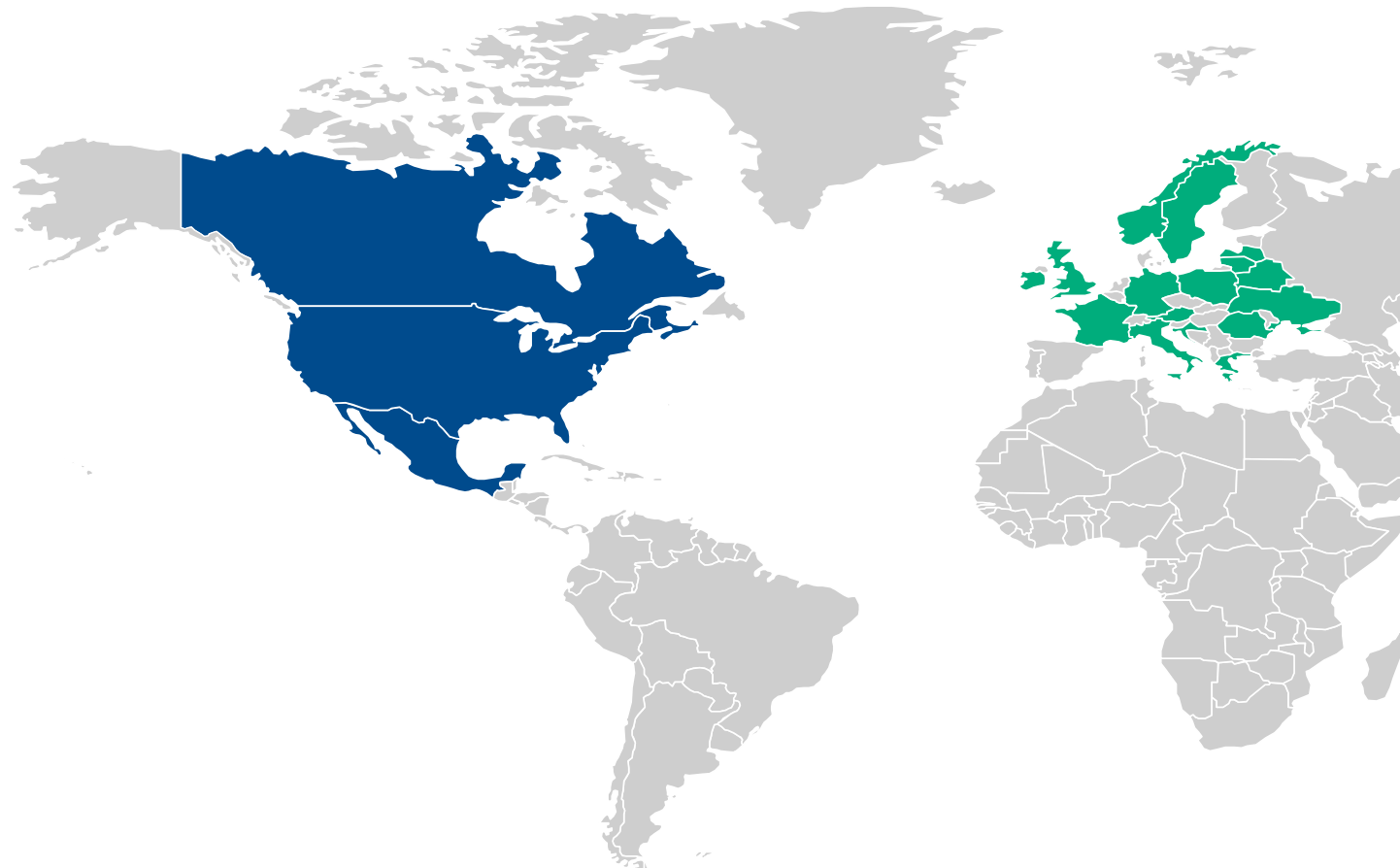
## North America

### Standards:

- API Chapter 6.X Supercritical Fluids (CO<sub>2</sub>)
- Measurement Canada - Development Committee for H<sub>2</sub> T&C

### Research Institute:

- NIST - Master Meter study, training, and tech support
- NCWM/NTEP NIST HB44 - Specifications and Tolerances



## Europe

### Regulations and Directive Development Connects us with Policy Makers and Coordinators for Technical Discussions

- Submit 3 amendments to directives and regulations on “Internal markets for renewable and natural gas for Hydrogen”
- Consult on major review proposal of Measuring Instrument Directives (MID) to address H<sub>2</sub> and CO<sub>2</sub> measurement gaps

### Joint Industry Projects

- Chairman of Advisory Board – MetHyInfra
- Advisory Board Member – MetCCUS
- Advisory Board Member – MetHyVE2
- Consortium Member – RHeadHy Project
- Consortium Member – H<sub>2</sub>FlowTrace
- DNV JIP CO<sub>2</sub>
- DNV JIP H<sub>2</sub>

### Standards Committees

- NEN (Netherlands Royal Standardization Institute)

### Industry Partnerships:

- Consultant to IGOP – CO<sub>2</sub> instrumentation

# Applications and Measurement in CCUS

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# CCUS Carbon Capture & Storage / CO<sub>2</sub> Transportation & Distribution Challenges with CO<sub>2</sub> measurement

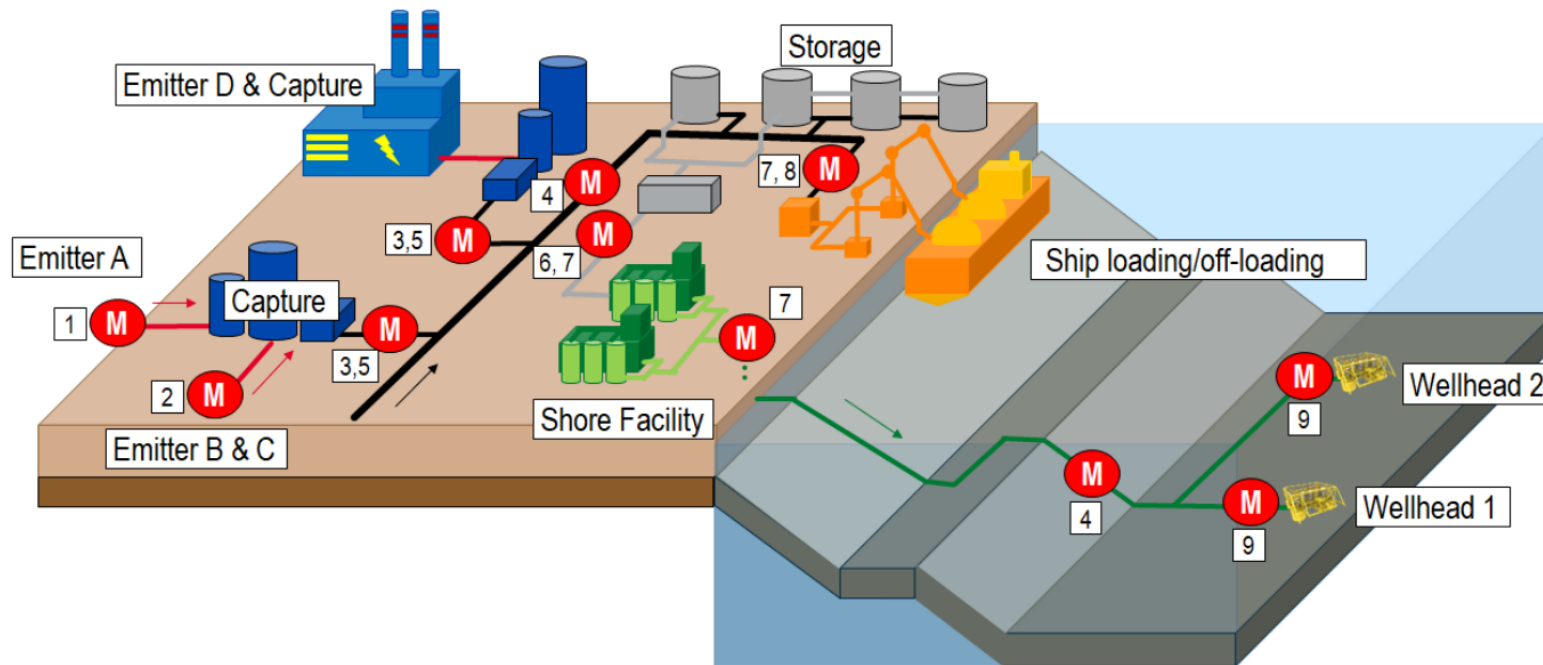
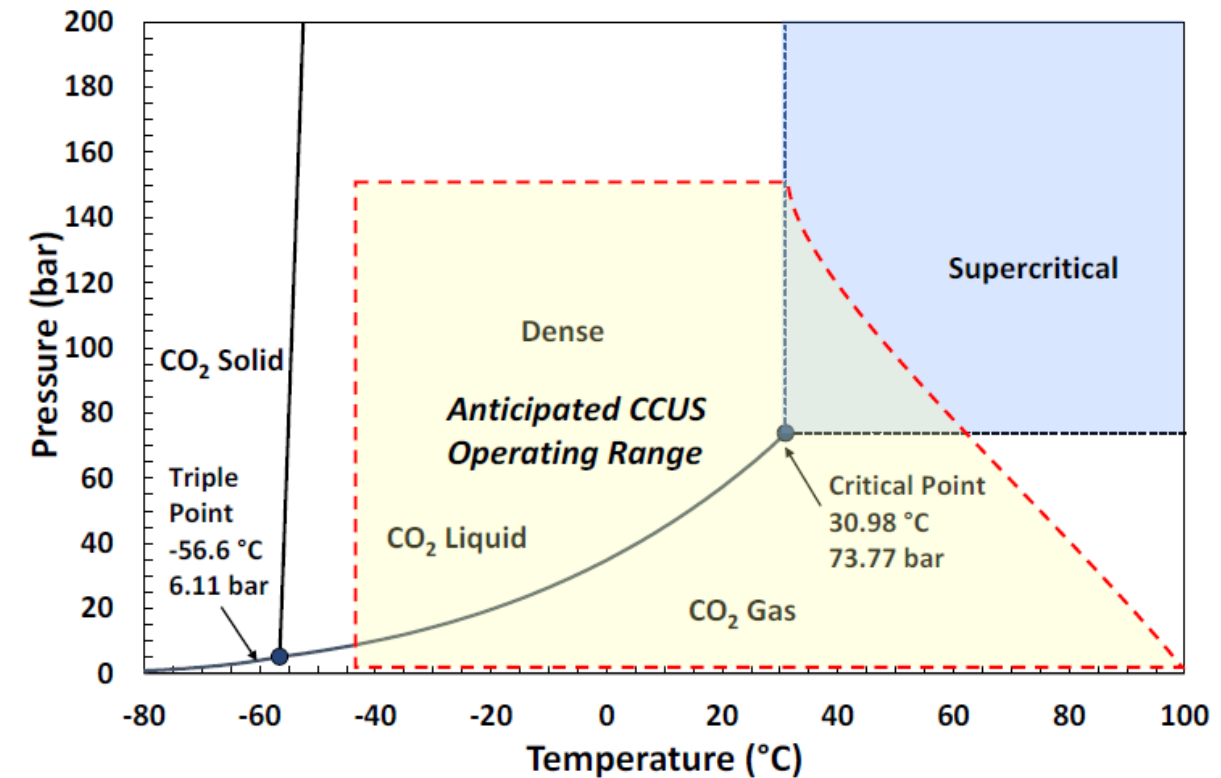


Figure 3: CCUS transportation measurement nodes. Adapted from [15]. For measurement node



- Gas at 1 bar and 20 °C
  - Compressibility effect on measurement
- small changes in temperature and pressure may result in large changes in fluid properties
- Impurities amplifies significant shifts in phase boundaries
- CO2 has acoustic attenuation
  - Not relevant to Coriolis

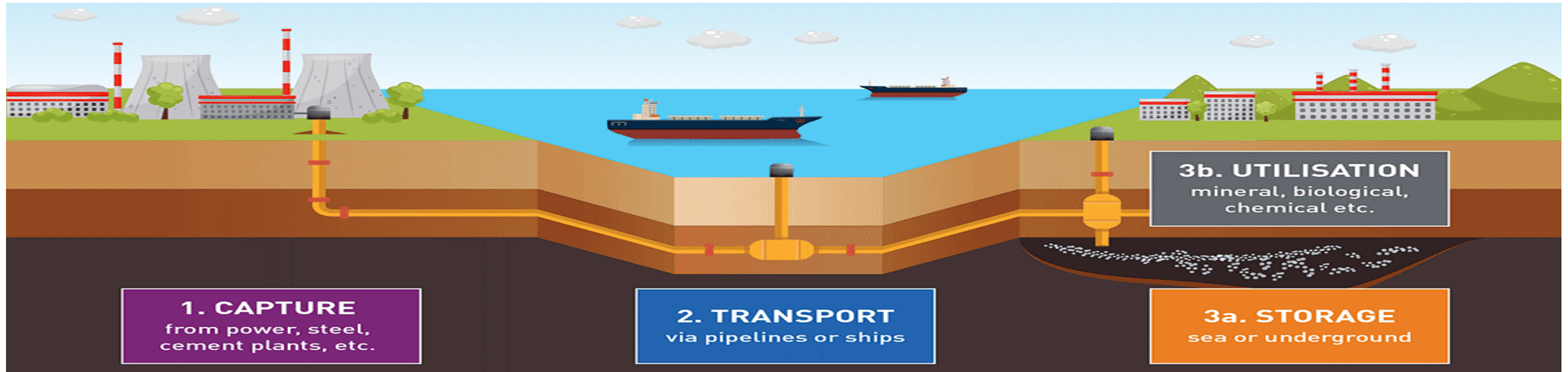
- Liquid at 57 bar and 20°C
- Supercritical at critical point of 31.1 °C and 73.9 bar
- small changes in temperature and pressure may result in large changes in fluid properties
- Impurities amplifies significant shifts in phase boundaries

Compressed Gas

Liquified CO<sub>2</sub>



# Typical CCUS Applications



## Production

- Models CMF300
- Pressure 36 Bars



## Tube Trailer Loading / Unloading

- Models Up to HC2
- Pressure Capture at 16 bars
- Transport at pressures > 100 bars



## Large Industrial Consumers

- Models CMF300 to HC4
- Pressure 15 bars
- Liquefied <math>< 50^{\circ}\text{C}</math>



Compressed Gas

Liquefied CO<sub>2</sub>

# Measuring Gaseous fluids with Coriolis

- Due to Compressibility of Gases, there is a potential shift in Mass measurement in Coriolis
- This is applicable to all gases measured by all Coriolis meters
- The error can be estimated and corrected based on a scientific method as described by Hemp and Kutin.

$$E_{\dot{m}} = \frac{1}{2} \left( \frac{\omega_1}{c} b \right)^2$$


Where:

$\omega_1$  is resonance frequency of the meter

$b$  is flowmeter tube inner radius


$c$  is velocity of sound through the gaseous fluid

**MicroMotion Coriolis Flow Meters  
has the lowest resonance  
frequency; therefore, the estimated  
error is much lower**



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Available online at [www.sciencedirect.com](http://www.sciencedirect.com)



ScienceDirect

Flow Measurement and Instrumentation 17 (2006) 359–369

**Flow Measurement  
and Instrumentation**

[www.elsevier.com/locate/flowmeasinst](http://www.elsevier.com/locate/flowmeasinst)

Theory of errors in Coriolis flowmeter readings due to compressibility of the fluid being metered

J. Hemp<sup>a,\*</sup>, J. Kutin<sup>b</sup>

<sup>a</sup> Wolfson College, Oxford OX2 6UD, UK  
<sup>b</sup> Laboratory of Measurements in Process Engineering, Faculty of Mechanical Engineering, University of Ljubljana, Aškerčeva 6, SI-1000 Ljubljana, Slovenia

Received 2 May 2006; received in revised form 24 July 2006; accepted 25 July 2006

Note: The referenced Hemp and Kutin paper describe the approach to estimate the error in a straight tube.

# Measuring Gaseous CO<sub>2</sub> with Coriolis

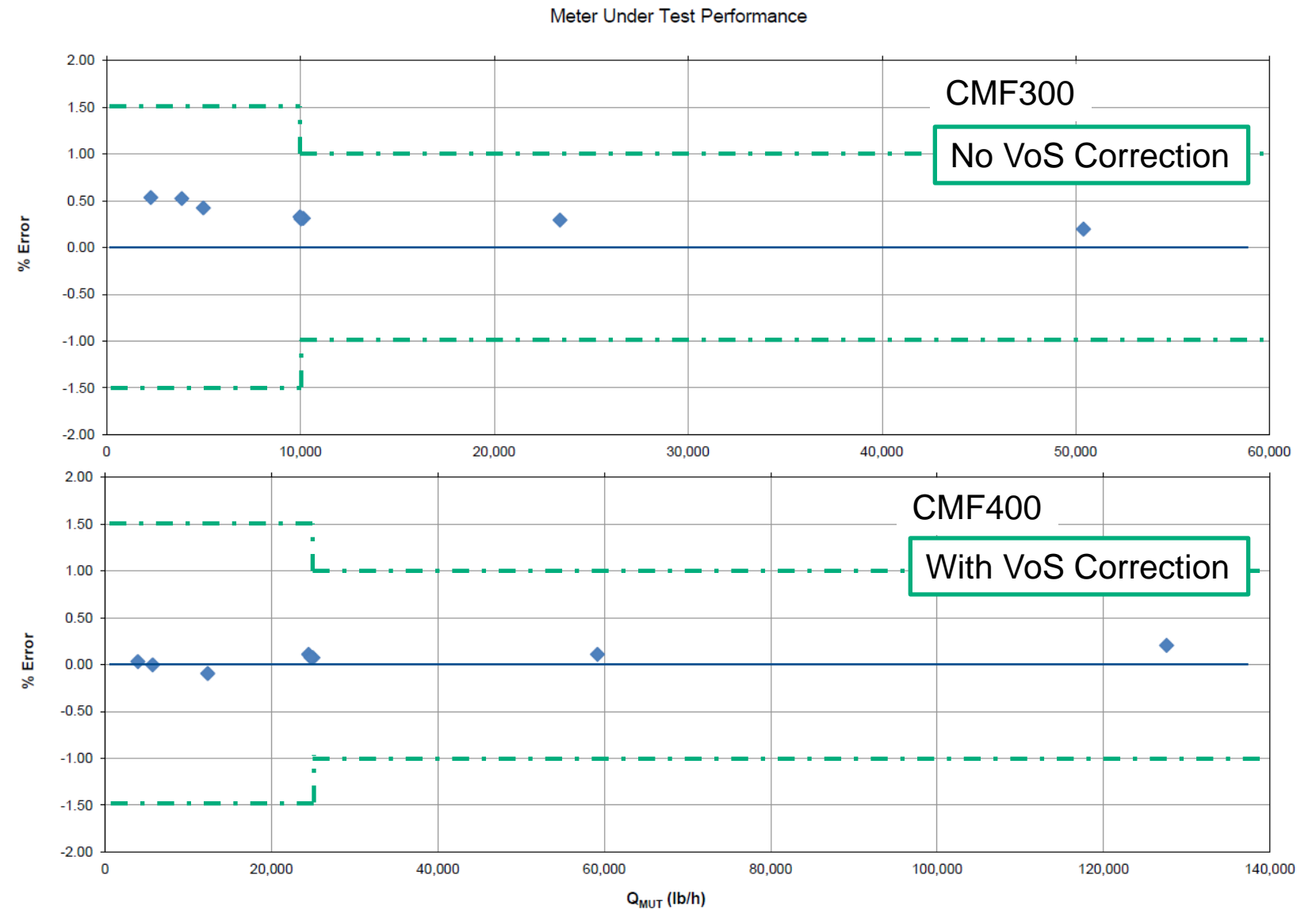
- The estimated error with CO<sub>2</sub> is attributed largely to the low Velocity of Sound (VoS) through the medium
- As with other gases, the error increases with larger meter sizes and negligible in smaller meter sizes

 *This effect is negligible or non-existent in smaller MicroMotion Coriolis flow meters*

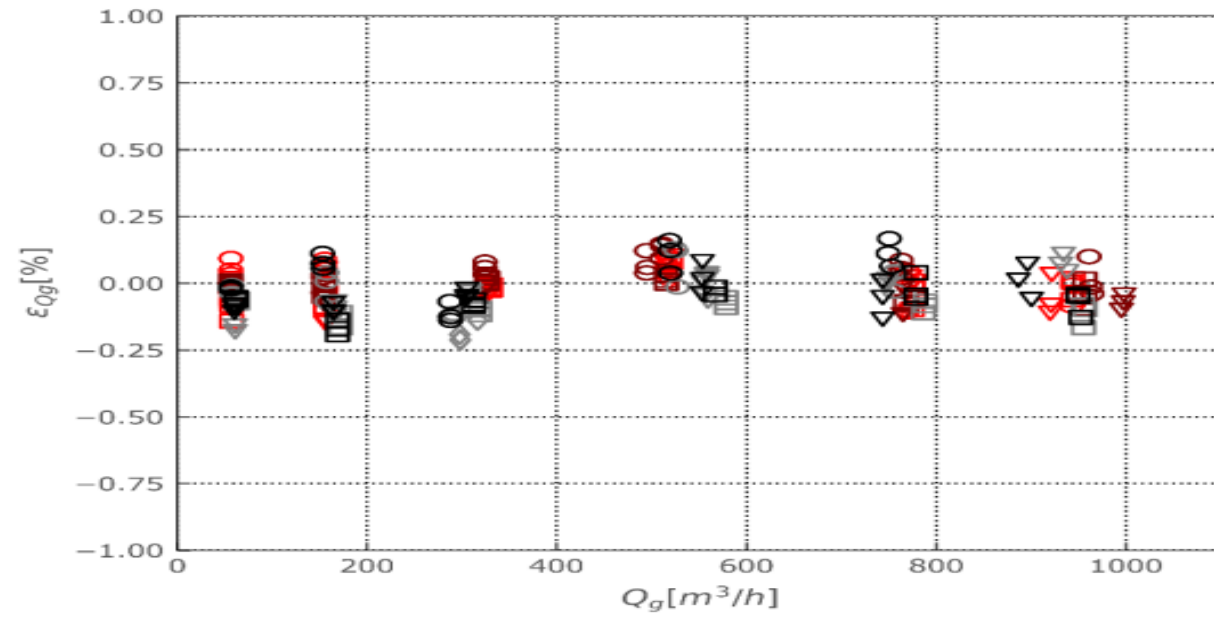
- Mass Error Correction is correlated to VoS
- VoS ( $c$ ) is extrapolated with Live measurement of:
  - Density
  - Temperature
  - Coriolis Operating Frequency

# Measuring Gaseous CO<sub>2</sub> with Coriolis

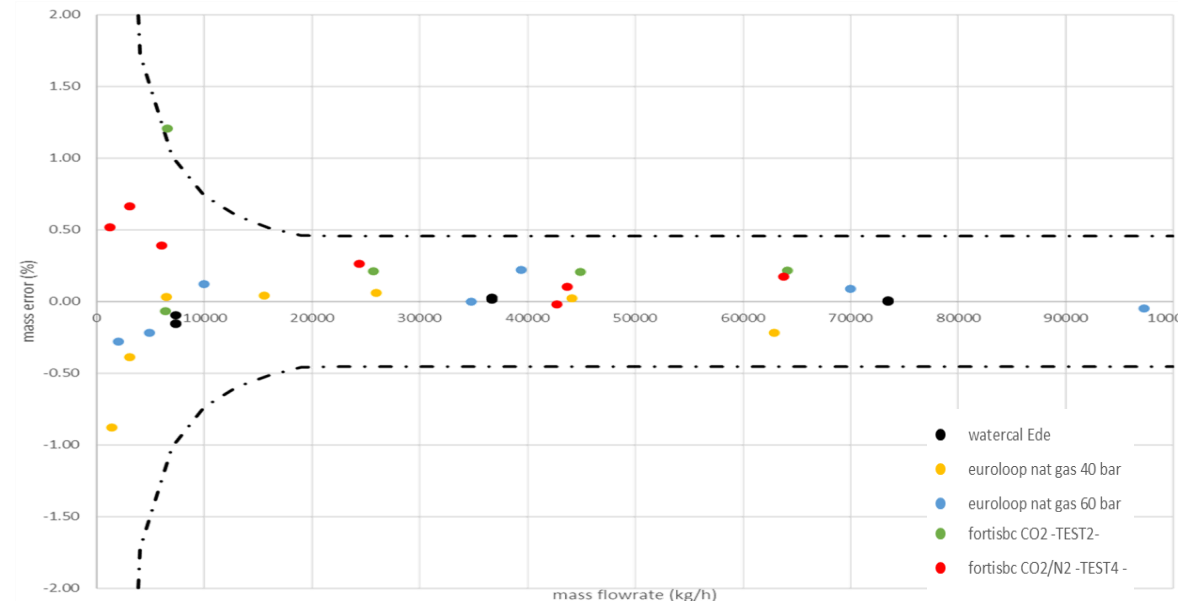
- As Found Calibration at FortisBC for CMF300 and CMF400
- Calibration on CO<sub>2</sub> done with same parameter settings as in water calibration
- Part of Type Approval testing with NMI for OIML R137 certification
- Performance is compliant with Accuracy class 0.5 and 1.0



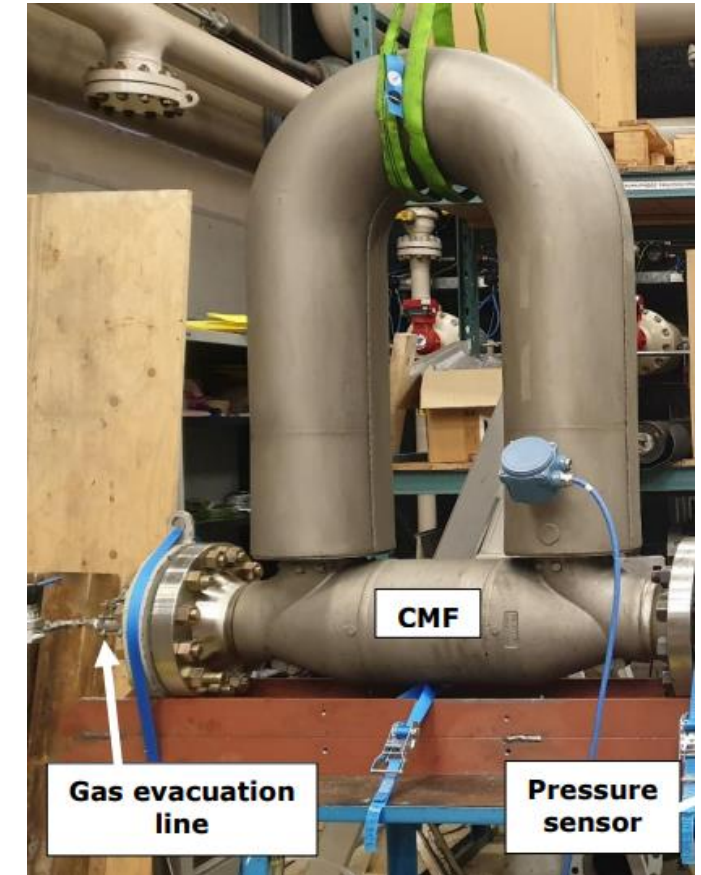
# Measuring CO<sub>2</sub> in Gas Phase with Impurities



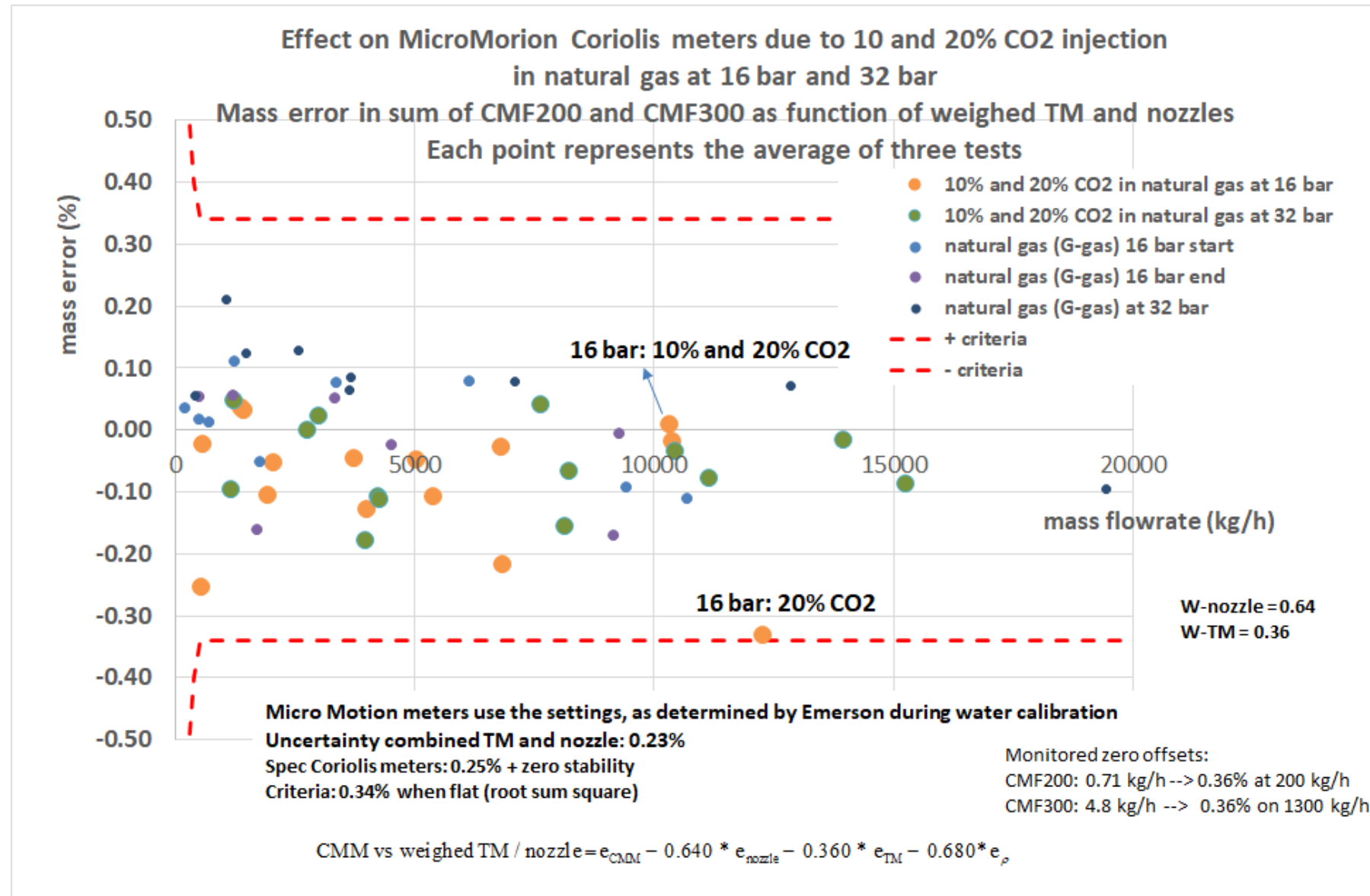
- $G_{gas_1} (p = 34\text{bar})$
- ▽  $G_{gas_1} (p = 25\text{bar})$
- $G_{gas_1} (p = 16\text{bar})$
- $G_{gas_2} (p = 34\text{bar})$
- ▽  $G_{gas_2} (p = 25\text{bar})$
- $G_{gas_2} (p = 16\text{bar})$
- $CO_2 \text{ 95\%} (p = 34\text{bar})$
- ▽  $CO_2 \text{ 95\%} (p = 25\text{bar})$
- $CO_2 \text{ 95\%} (p = 16\text{bar})$
- ◇  $CO_2 \text{ 95\%} (p = 6\text{bar})$
- $CO_2 \text{ 99\%} (p = 34\text{bar})$
- ▽  $CO_2 \text{ 99\%} (p = 25\text{bar})$
- $CO_2 \text{ 99\%} (p = 16\text{bar})$



- watercal Ede
- euroloop nat gas 40 bar
- euroloop nat gas 60 bar
- fortisbc CO<sub>2</sub>-TEST2-
- fortisbc CO<sub>2</sub>/N<sub>2</sub>-TEST4-



# Measuring CO<sub>2</sub> injection up to 20% with Coriolis



## Natural Gas with CO<sub>2</sub> injection up till 20% at 16 and 32 bar

- Mass errors assessed to a criteria of 0.34%
- Population is within uncertainty criteria of 0.34%
- Presented results based on water settings

# **Prove of Transferability and Traceability**

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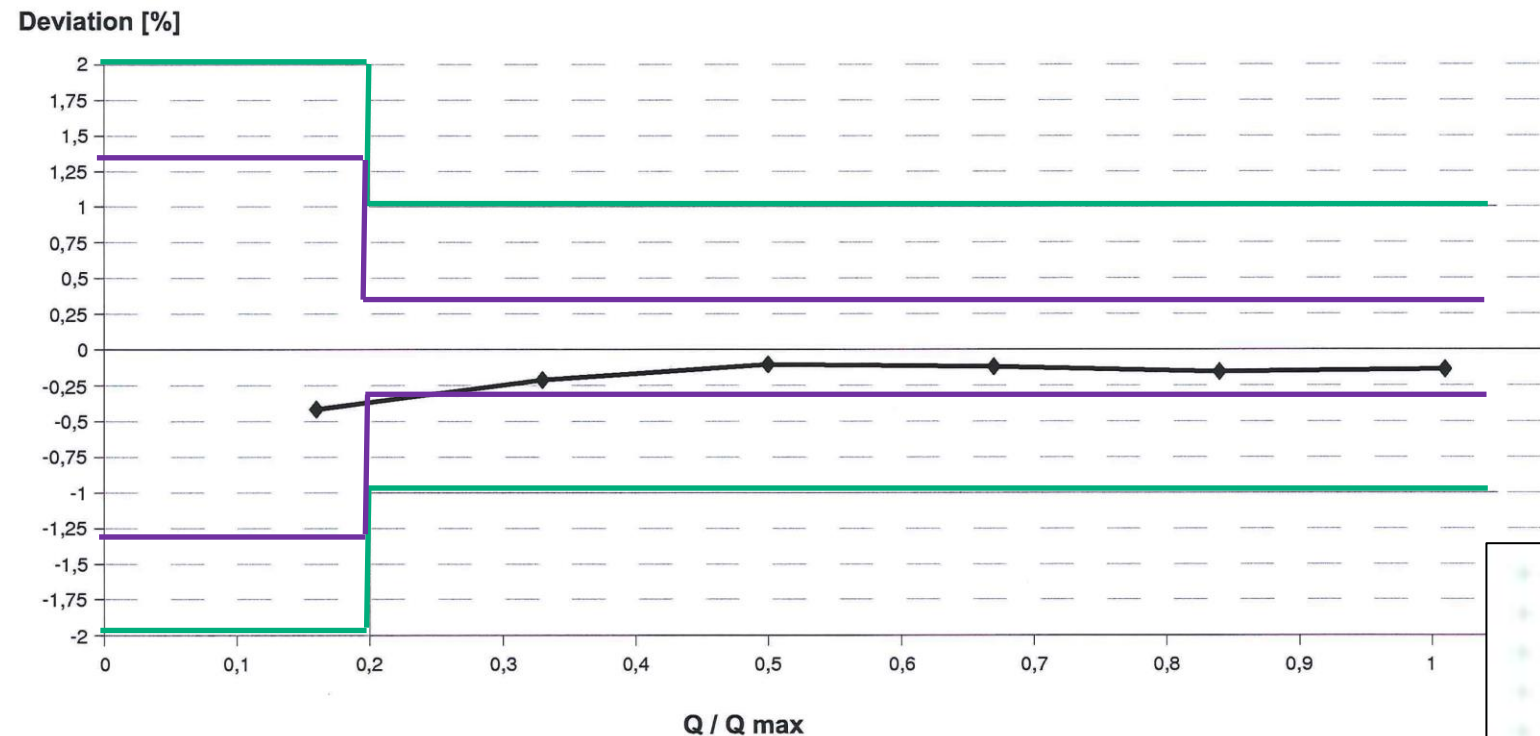
# Water Transferability – Approach & Certification

**STEP 1:** New meter with no FCF

**STEP 2:** Establish FCF through water calibration

**STEP 3:** Verify on other gases with FCF (established in STEP 2)

**STEP 4:** Verify MPE according to table in NMI Statement



## DECLARATION

Number NMI-SO14200852-04  
Page 1 of 2  
Project number SO14200852

**Issued by:** NMI Certin B.V.  
Hugo de Grootplein 1  
3314 EG Dordrecht  
The Netherlands

**Applicant:** Emerson Process Management Flow B.V.  
Neonstraat 1  
6718 WX Ede  
The Netherlands

**Submitted:** Coriolis meters  
Manufacturer : Micro Motion  
Sensor Models : CMF025, CMF050, CNG050, CMF100, CMF200, CMF300, CMF350, CMF400, CMFHC2, CMFHC3 and CMFHC4

**Scope of investigation:** Investigation of the Micro Motion coriolis meters, model CMF025, CMF050, CNG050, CMF100, CMF200, CMF300, CMF350, CMF400, CMFHC2, CMFHC3 and CMFHC4 with both water and natural gas or nitrogen as medium. The background of the investigation is to find out whether those meters can be used for custody transfer purposes with a certain gas, while they are verified with water, without testing them with that particular gas.

**Tests:** With several meters of the above mentioned models an accuracy test is performed with water. After that the accuracy test is repeated with natural gas or nitrogen, under high pressure. During both tests each meter is programmed with the same calibration parameter (FlowCal factor)

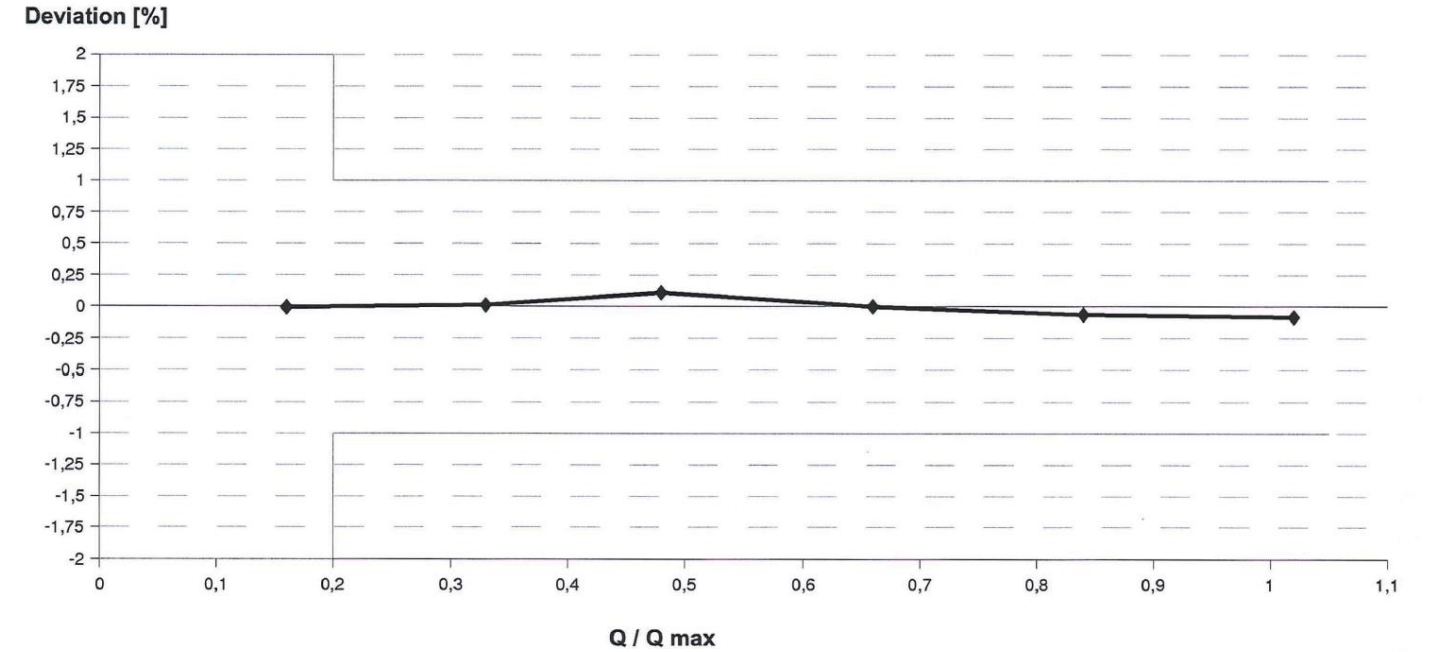
**Result:** The maximum measured difference between both accuracy tests is 0,5% for all above mentioned sensor models, except for the CMF025 where 0,6% is found. Concerning this maximum measured difference, while adding an extra safety margin the verification of the coriolis meters may be performed with water, without testing them with the particular gas, when using the maximum permissible errors with water, as stated in the table below.

Flow range	Maximum permissible errors with gas	Maximum permissible errors with water
$Q_{min} - 0,2 Q_{max}$	± 2,0%	± 1,3%
$0,2 Q_{max} - Q_{max}$	± 1,0%	± 0,3%



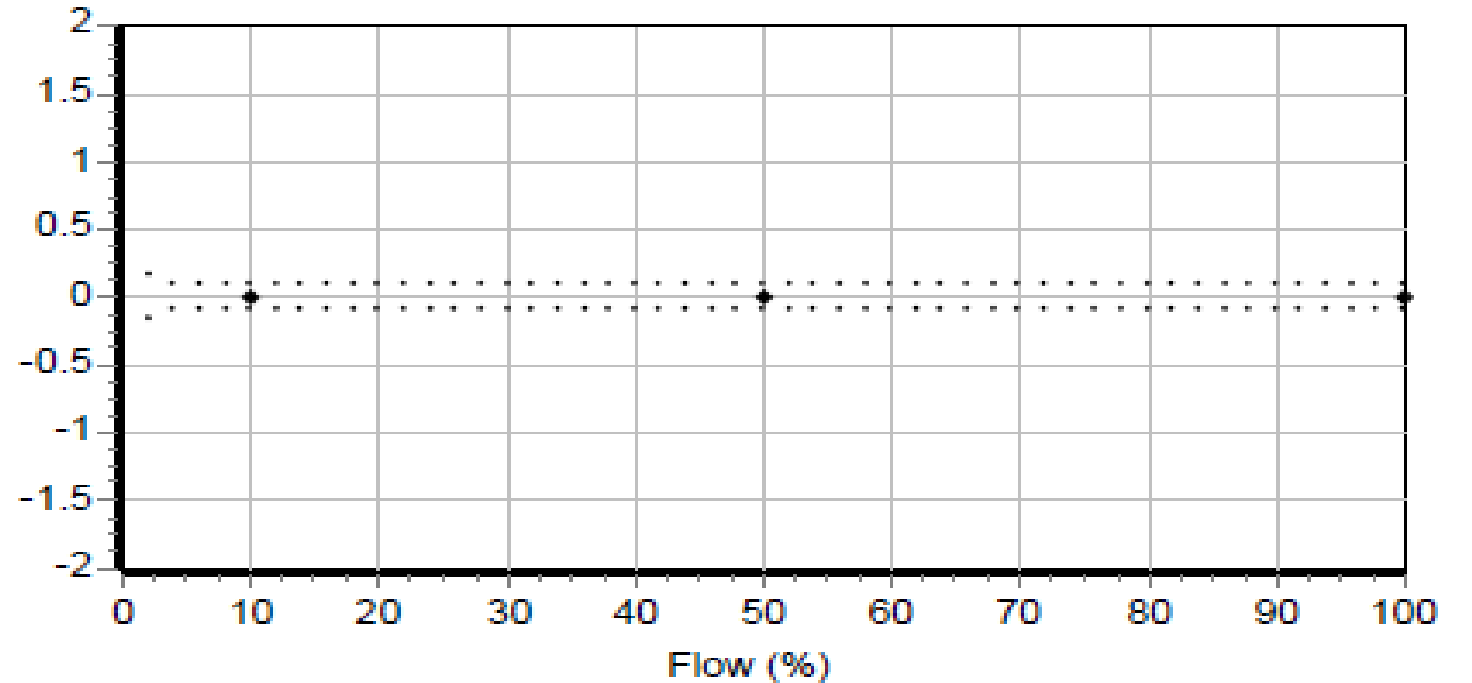
# Water Transferability – Example Natural Gas CMF300

Results (as left)	Qi / Qmax	Qi (kg/h)	Reynoldsnnumber	Deviation (%)	n	U <sub>meter</sub> (%)	U <sub>tot</sub> (%)
	0,16	634,23	0,20 *10 <sup>6</sup>	-0,01	4	0,09	0,25
	0,33	1303,60	0,41 *10 <sup>6</sup>	0,01	4	0,13	0,26
	0,48	1903,45	0,59 *10 <sup>6</sup>	0,11	3	0,03	0,23
	0,66	2623,26	0,81 *10 <sup>6</sup>	0,00	3	0,03	0,23
	0,84	3358,17	1,04 *10 <sup>6</sup>	-0,06	4	0,04	0,23
	1,02	4065,73	1,26 *10 <sup>6</sup>	-0,08	3	0,00	0,23



Note: calibration on Natural Gas done with same parameter settings as in water calibration

Flow (%)	Flow Rate (kg/min)	Meter Total (kg)	Reference Total (kg)	Error (%)	Specification (±%)
100.0	2268	2250.083	2250.149	-0.003	0.100
10.0	226.8	511.1505	511.1675	-0.003	0.100
50.0	1134	1117.784	1117.797	-0.001	0.100
100.0	2268	2250.083	2250.098	-0.001	0.100



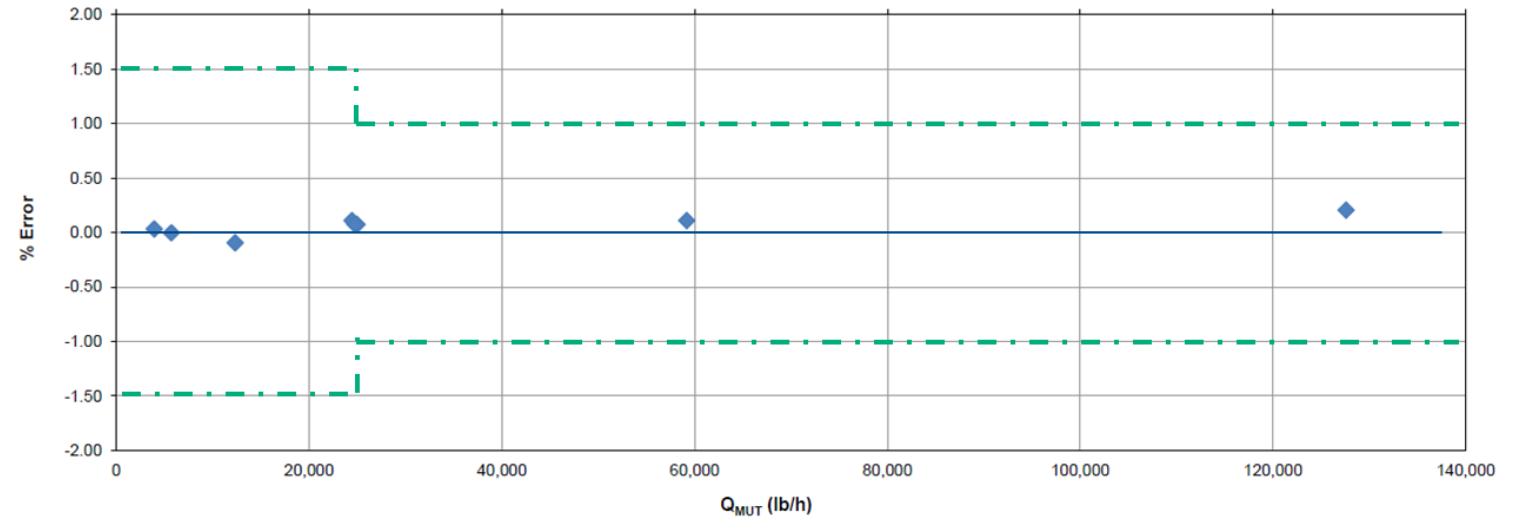
\* Water Calibration uncertainty of ±0.03%

# Water Transferability – Example CO<sub>2</sub> CMF400

Configuration File  Customer Config  As Found  As Left  Final Config  
Data File

Test Point	P <sub>REF</sub> (psia)	T <sub>REF</sub> (°F)	Density <sub>REF</sub> (lb/ft <sup>3</sup> )	Q <sub>REF</sub> (lb/h)	Q <sub>MUT</sub> (lb/h)	% Error HF	K-Factor pulses/lb	CMC (%)	Utot (%)
1	240.1	73.6	2.0276	127,276	127,533	0.20	136.3523	0.29	0.32
2	240.0	71.3	2.0394	59,080	59,143	0.11	136.2245	0.29	0.30
3	240.1	75.6	2.0177	24,935	24,954	0.07	136.1767	0.29	0.29
4	240.0	78.0	2.0049	12,309	12,297	-0.10	135.9463	0.29	0.30
5	239.4	79.3	1.9925	5,696	5,695	-0.01	136.0700	0.29	0.30
6	238.7	80.5	1.9807	3,893	3,894	0.03	136.1168	0.29	0.29
7	238.9	82.4	1.9729	24,405	24,431	0.11	136.2233	0.29	0.29
8	240.4	80.2	1.9972	24,725	24,742	0.07	136.1740	0.29	0.29

Table 1 Meter Calibration Results

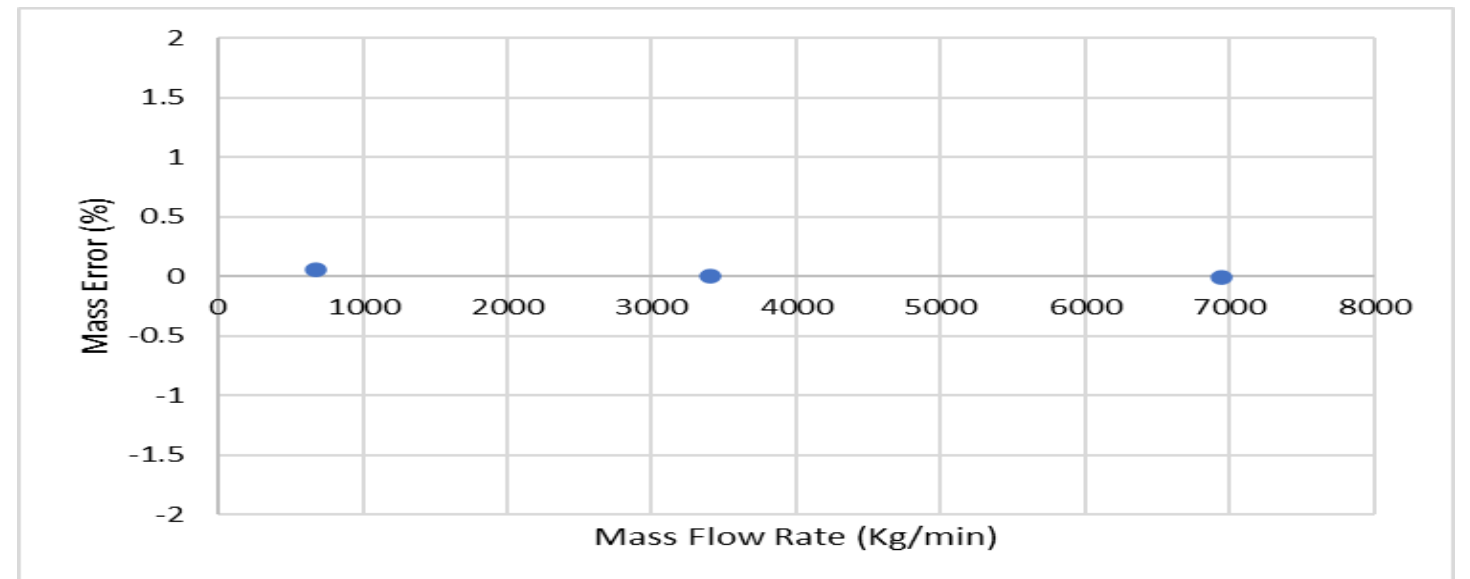


Note: calibration on CO<sub>2</sub> gas done with same parameter settings as in water calibration

Average Calibration Results for Meter Under Test

Grp	Mass Rate (kg/min)	Mass Total (kg)	Mass Error (%)	Volume Rate (l/min)	Volume Total (l)	Volume Error (%)	Density (kg/m <sup>3</sup> )
1	6944	6950.853	-0.005	6961	6967.753	-0.019	997.575
2	672.3	673.2936	0.060	674.0	675.0061	0.057	997.463
3	3405	3408.634	0.004	3414	3417.365	0.001	997.445

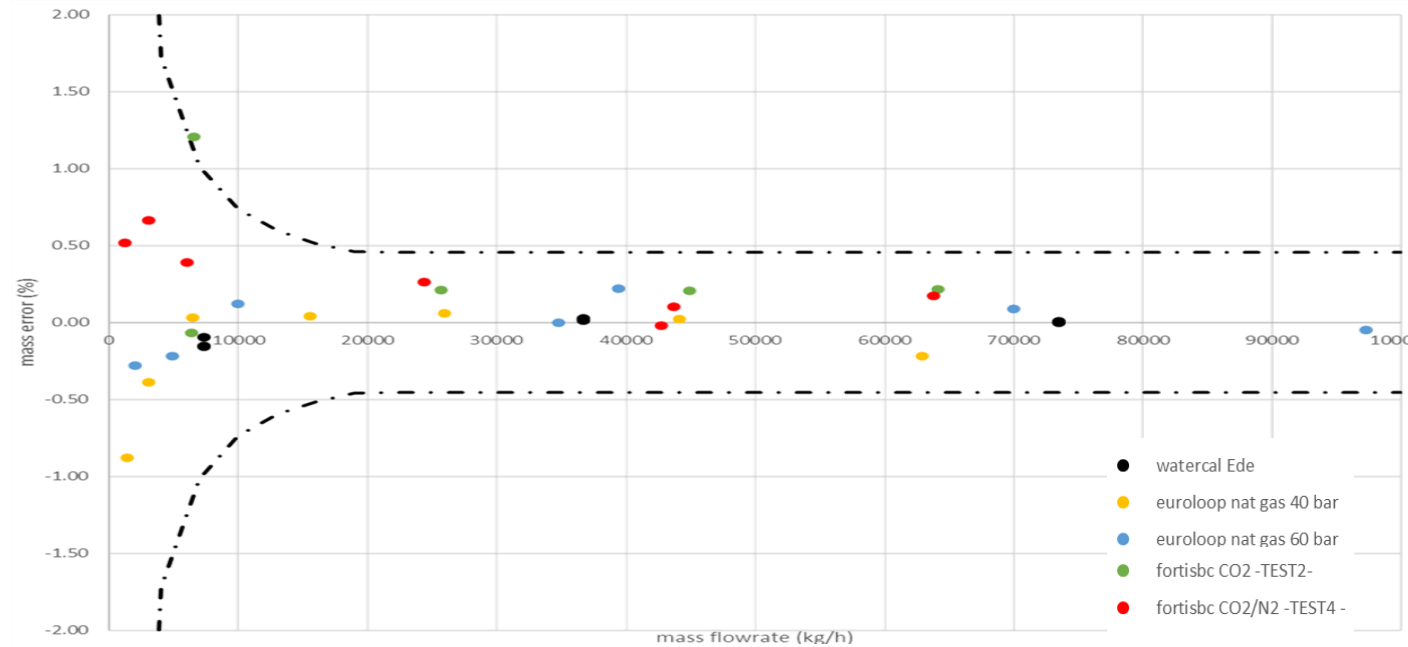
\* Water Calibration uncertainty of ±0.03%



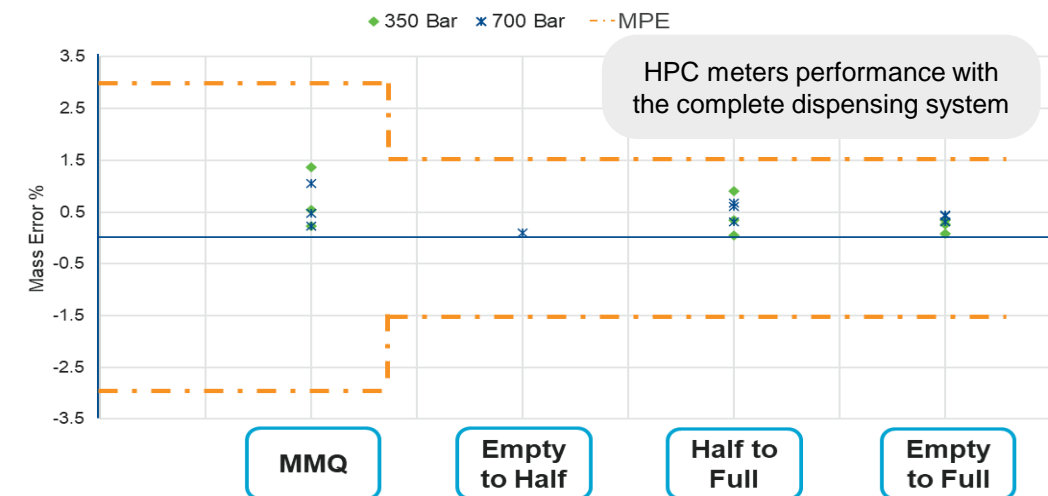
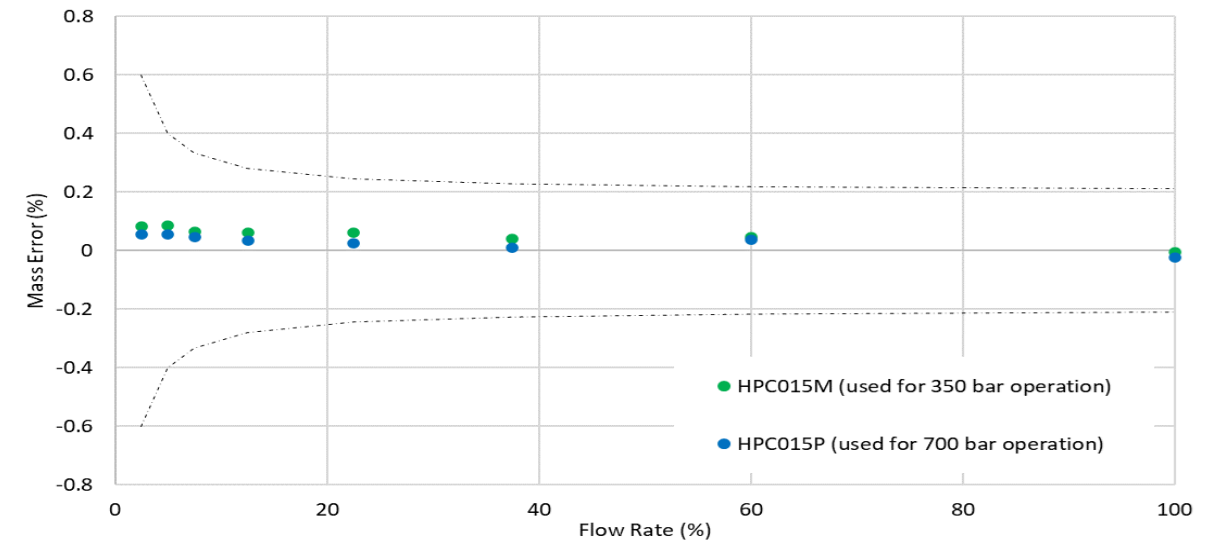
# Water Transferability for the H<sub>2</sub> and CCUS Economy

## CO<sub>2</sub> performance transferability from Water and Other gases

- Calibration on CO<sub>2</sub> with impurities (90% to 100% CO<sub>2</sub>)
- Calibration on NG
- Calibration on Water
- Performance within Class 0.5 for gas meters (OIML R137)



## H<sub>2</sub> performance transferability from Water



# Summary

- Coriolis Flow Meter are Fit for Purpose:
  - H<sub>2</sub> applications
  - CO<sub>2</sub> applications
- On-going work to build traceability facilities for H<sub>2</sub> and CO<sub>2</sub> Economy
  - Consideration for transferability from Water and Alternative Gases
- Coverage of Standards on H<sub>2</sub> and CO<sub>2</sub> is limited but OIML offers the best Fit

[IQ?]

**Stay Connected,  
Stay Safe**

---

[metrologyeurope-msol@emerson.com](mailto:metrologyeurope-msol@emerson.com)



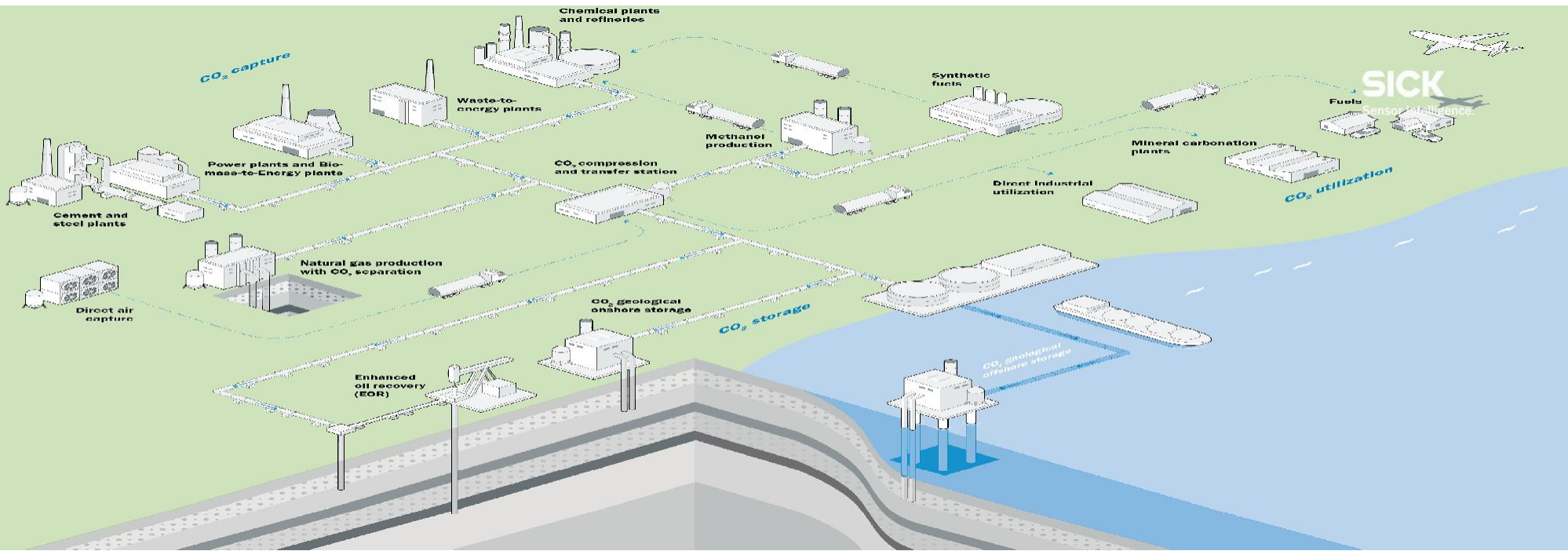
**CO<sub>2</sub> Measurement needs along the  
CCUS Value Chain**

Aurélie Moll  
Head of Industry Group Energy & CCUS

26.10.2023

# Agenda

1. Introduction
2. Decarbonization and CCUS Market trend
3. Sensor Solutions for the CCUS Value Chain



# 1. Introduction



# SICK at a glance

Key figures (fiscal year 2022)



# Process automation business fields

## Overview



Building



**CCUS** is a key milestone to support the **decarbonization** in those industries



Metals & Mining



Oil and gas



Power



Waste and Recycling

# Wide product and technology portfolio

Innovative portfolio from our Global Business Centers



PRESENCE  
DETECTION



INDUSTRIAL  
SAFETY



ANALYZERS



FLOW  
MEASUREMENT



SYSTEMS



INDUSTRIAL  
INTEGRATION SPACE



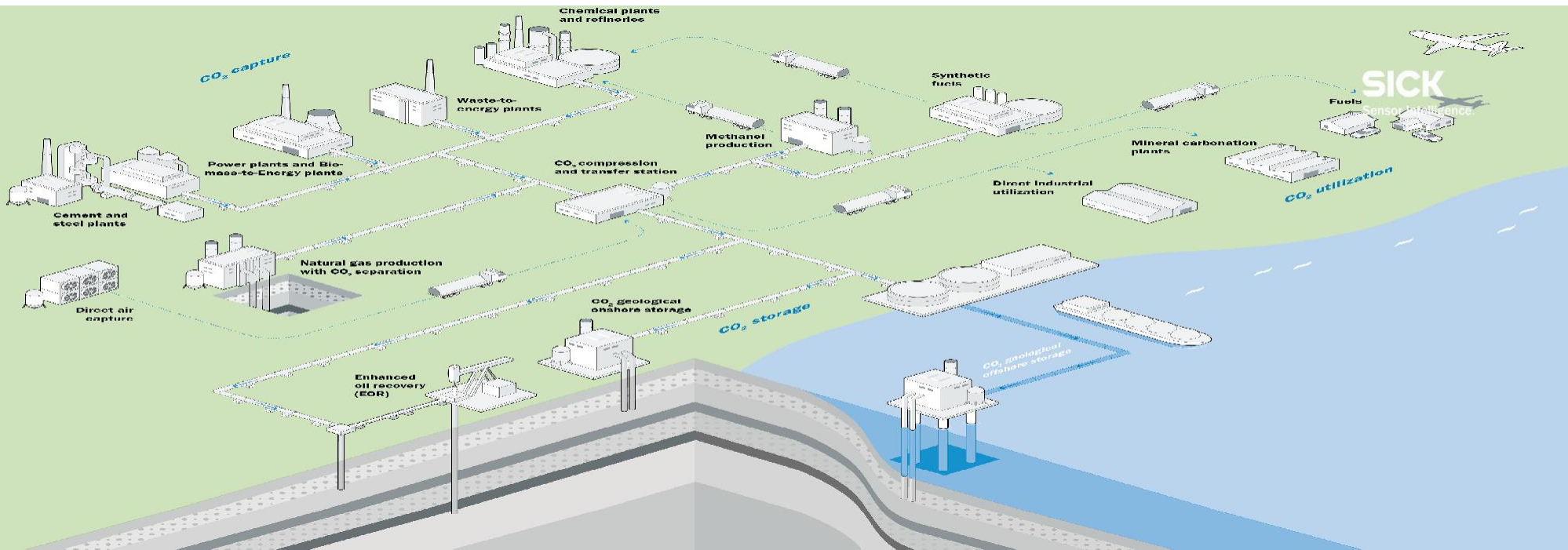
MOTION CONTROL  
SENSORS



IDENTIFICATION &  
MEASURING



NEW BUSINESS



## 2. Decarbonization and CCUS Market Trend

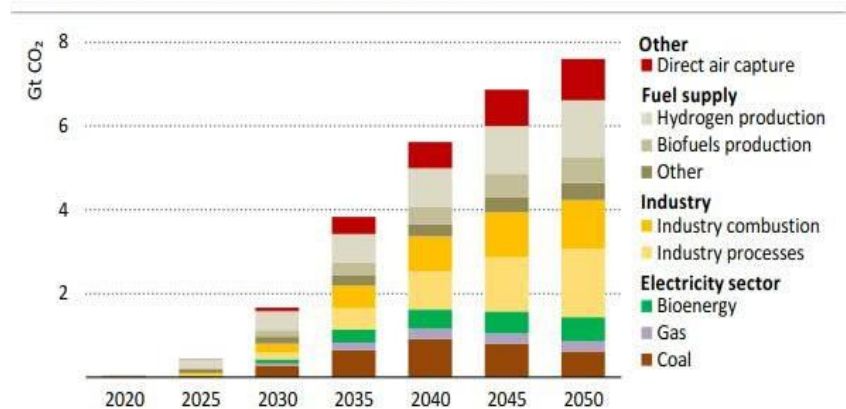
# Carbon Capture Utilization and Storage

## CCUS and Decarbonization

**Net Zero Emissions 2050 is only achievable by using CCUS**  
to offset for remaining emissions

- > **The IPCC Sixth Assessment Report 08/2021**
  - Temperatures expected to reach **1.5°C earlier than anticipated**
  - **Carbon dioxide removal** to compensate for residual CO<sub>2</sub> emissions to reach net zero or generate net negative CO<sub>2</sub> emissions
- > **IEA Net zero by 2050 - A Roadmap for the Global Energy Sector**  
Needed CCUS capacity to reach the climate targets  
**2030: 1,7 Gt CO<sub>2</sub>/year (7,6 Gt in 2050)**
- > **Policies Regulations: i.e. Europe “Fit for 55” EU Target 2030**  
Climate targets : **55% GHG emission reduction until 2030**
- > **CO<sub>2</sub> price and tax/credit systems**  
i.e. in Europe: EU ETS huge growth
- > **High Private-public funding in Billions €**

**Figure 2.21** ▶ Global CO<sub>2</sub> capture by source in the NZE



IEA. All rights reserved.



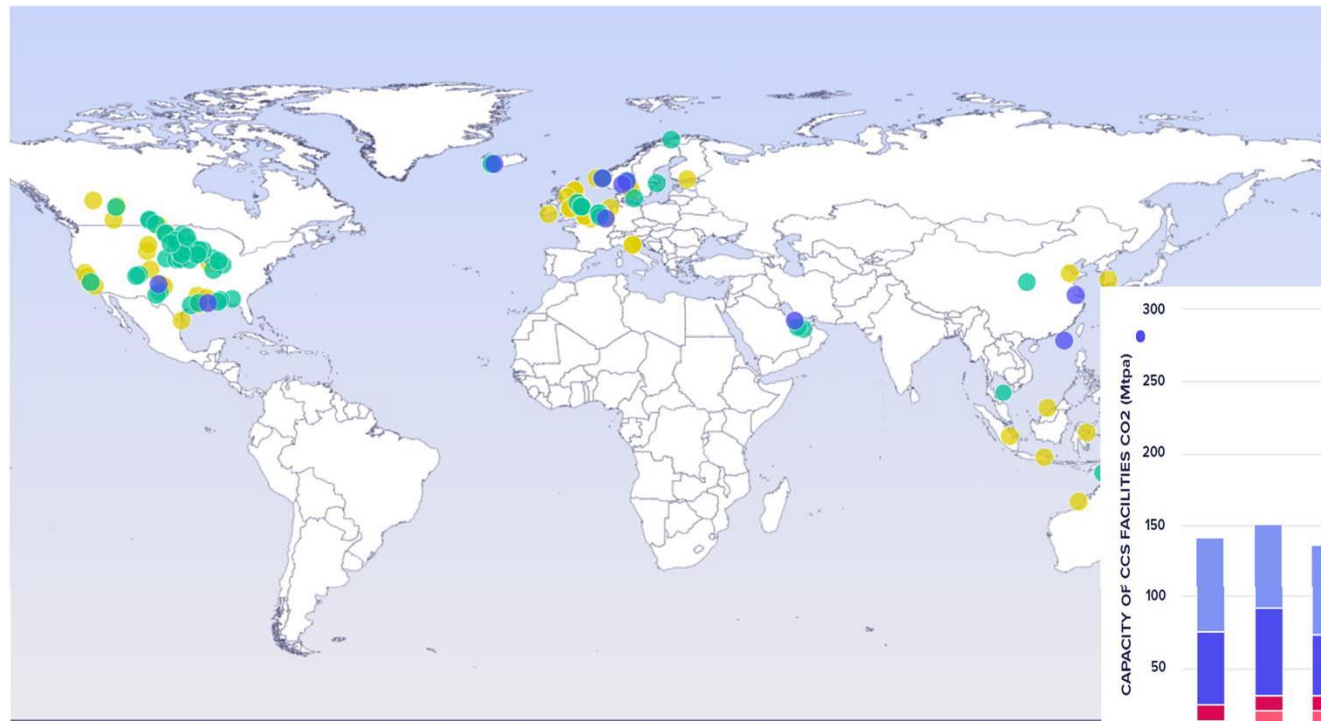
Confidential

# CCUS Market Trend

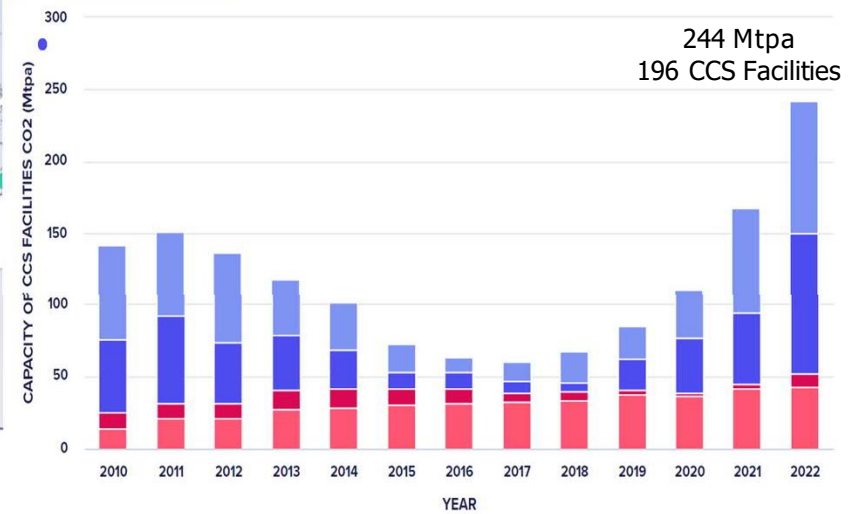
GCCSI – CCS Status Report 2022



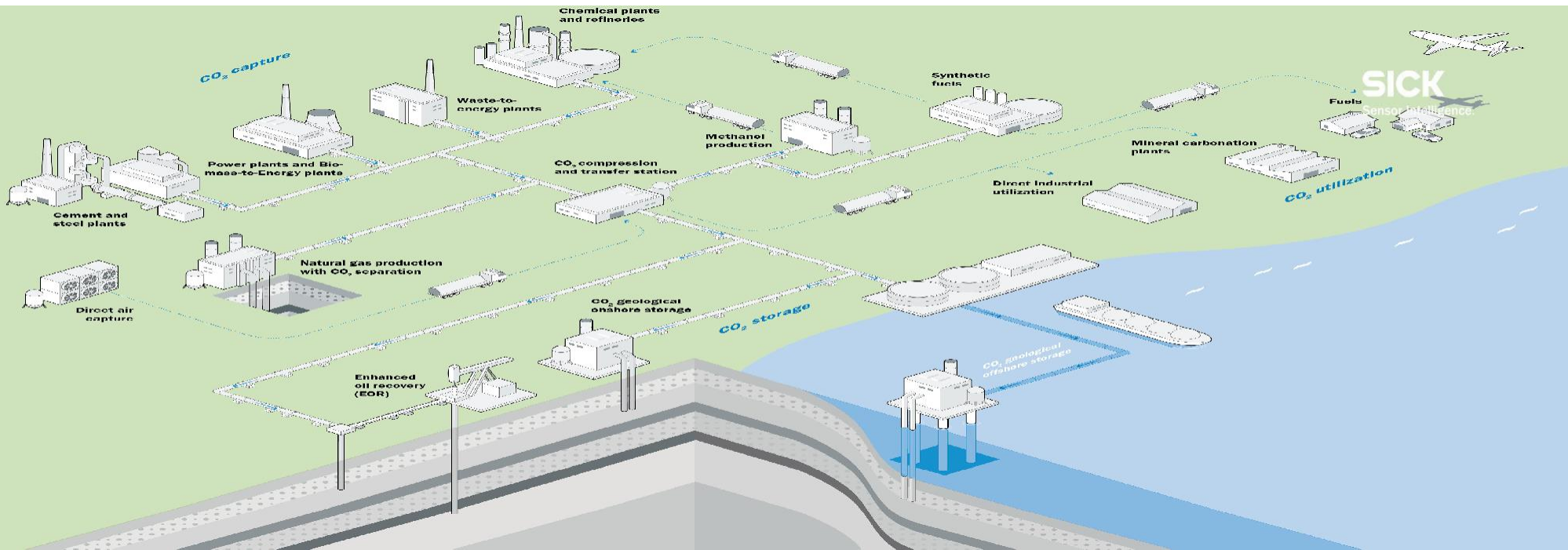
**GCCSI Status report 2022:**  
*commercial facilities since 2010 by capture capacity (Mtpa)*



● EARLY DEVELOPMENT ● ADVANCED DEVELOPMENT ● IN CONSTRUCTION



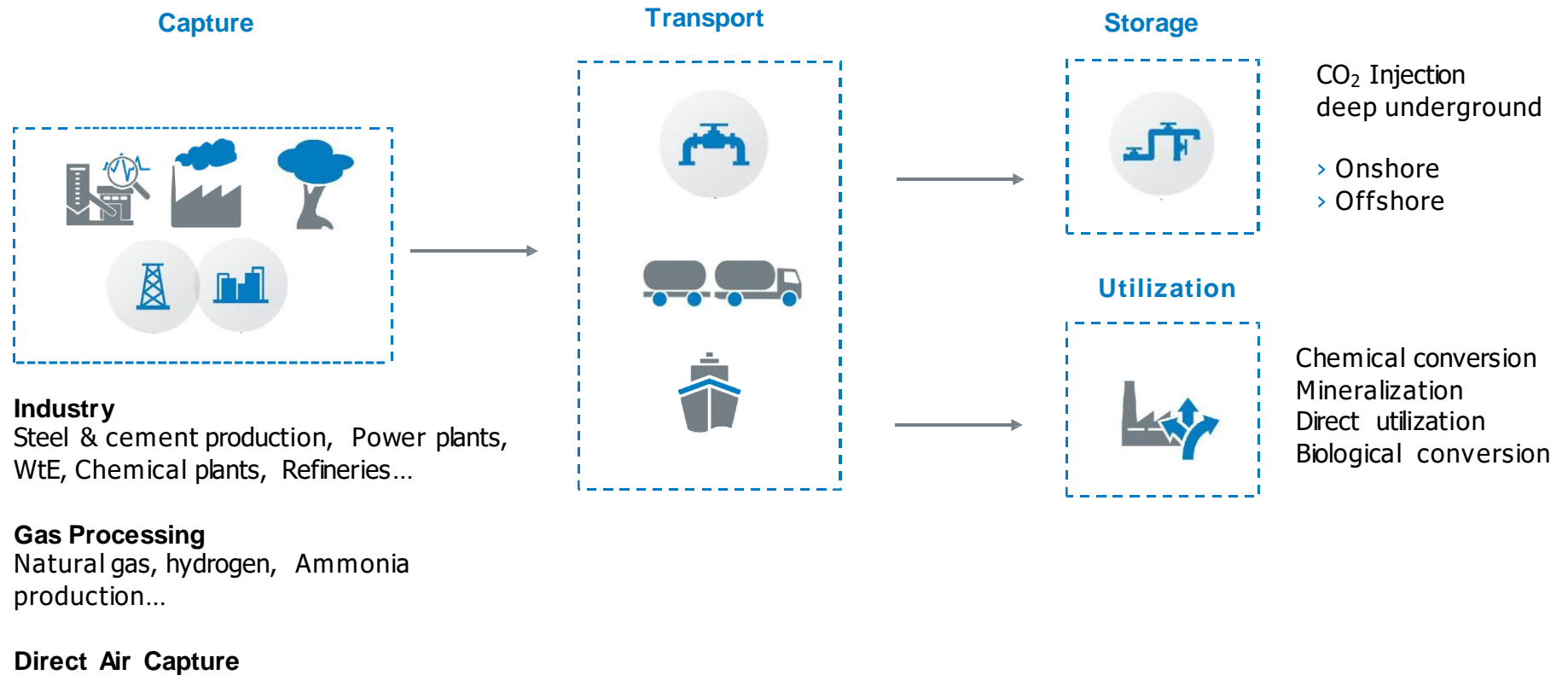
● EARLY DEVELOPMENT ● ADVANCED DEVELOPMENT ● IN CONSTRUCTION ● OPERATIONAL



### 3. SICK Sensor Solutions for the CCUS Value Chain

# Carbon capture utilization and storage

CCUS Value chain





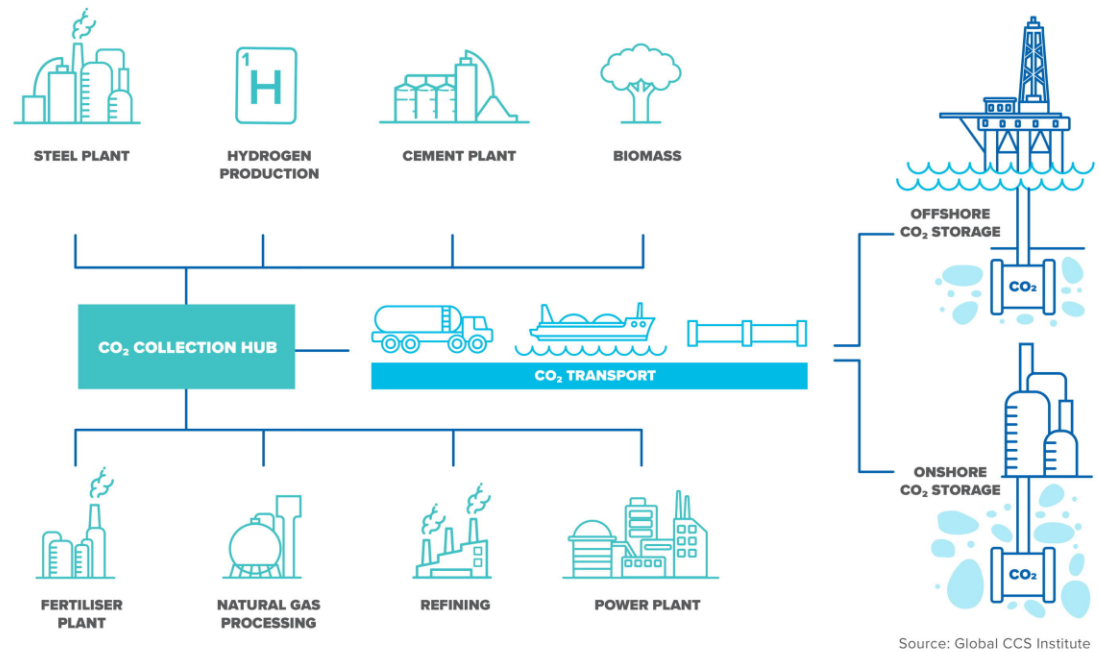
# Carbon capture utilization and storage

## Development of CCUS Networks

### Development of hubs and clusters in industrial areas

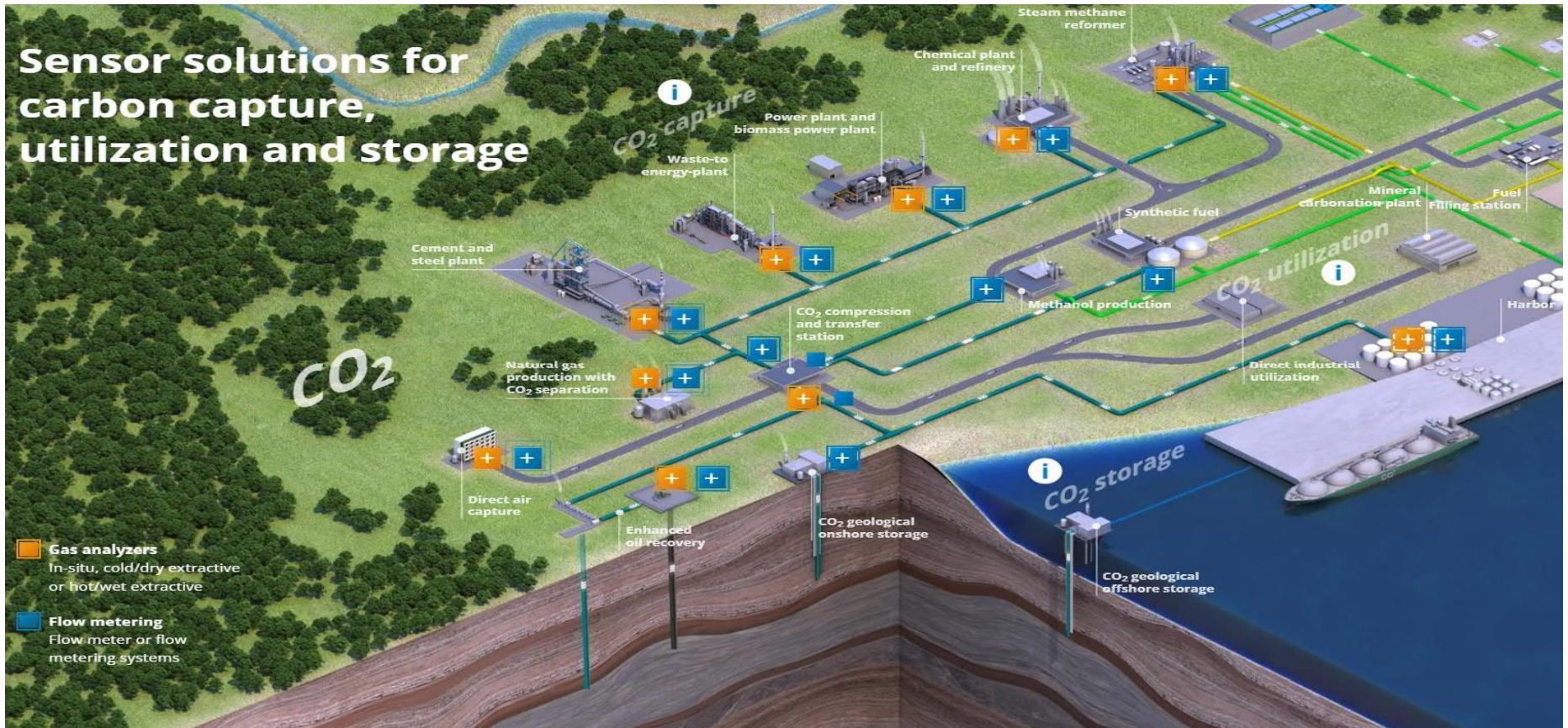
- > Proximity of industrial emitters
- > Common use of existing infrastructure
  - Pipelines
  - Industrial harbours
- > Construction of new common infrastructure
- > Cost optimization

### Need for precise and continuous CO<sub>2</sub> Measurement!



# CCUS Value Chain

Analyzer and Flowmeter solutions



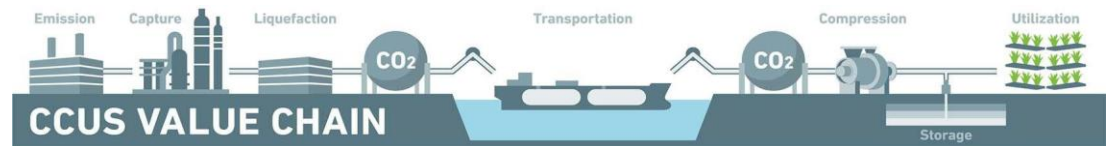
# SICK Solutions for the CCUS Value Chain

CO<sub>2</sub> Flow Metering & Gas Analysis



## SICK Solutions for the CCUS Value Chain

- > **Capture efficiency** with CO<sub>2</sub> concentration
- > **Quality** control (impurities)
- > **Reporting** (removed CO<sub>2</sub> quantity)



Source MHI Group

## Gas & Dust analyzers

- Single component analyzer (i.e. CO<sub>2</sub>) with insitu technology
- Quality / Impurity measurement with Multicomponent extractive analyzers
- Dust analyzers for dry & wet gases



Insitu analyzers



Multi-component extractive analyzers



Dust analyzers

## Flowmeters

- Ultrasonic Flowmeters



## Integrated Measuring Systems

- Metering skids
- Analyzer shelters



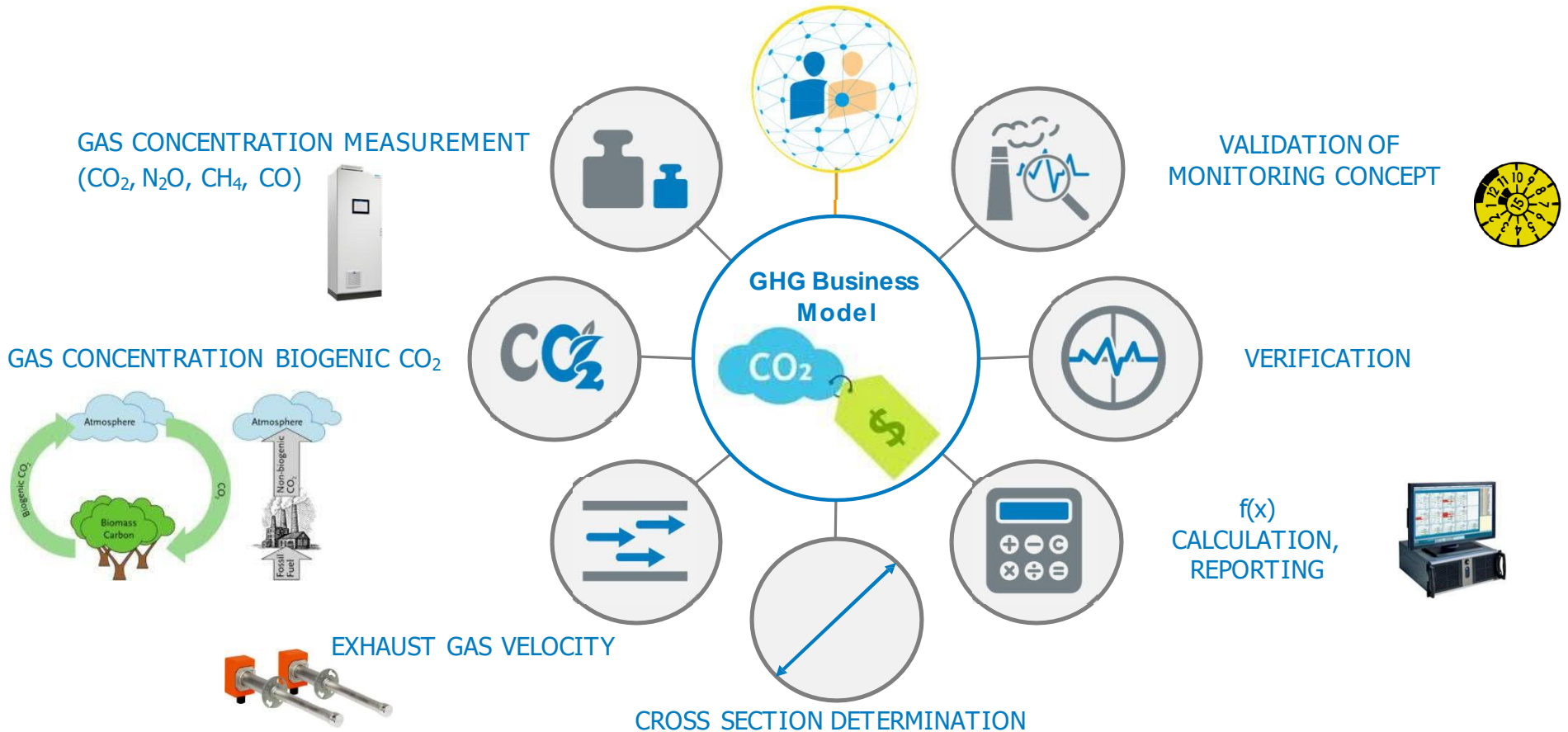
# SICK Solutions for the CCUS Value Chain

GHG Complete solution incl. digitalization



**SICK**  
Sensor Intelligence.

**ONE SEAMLESS CUSTOMER EXPERIENCE**



## SICK Solutions for the CCUS Value Chain

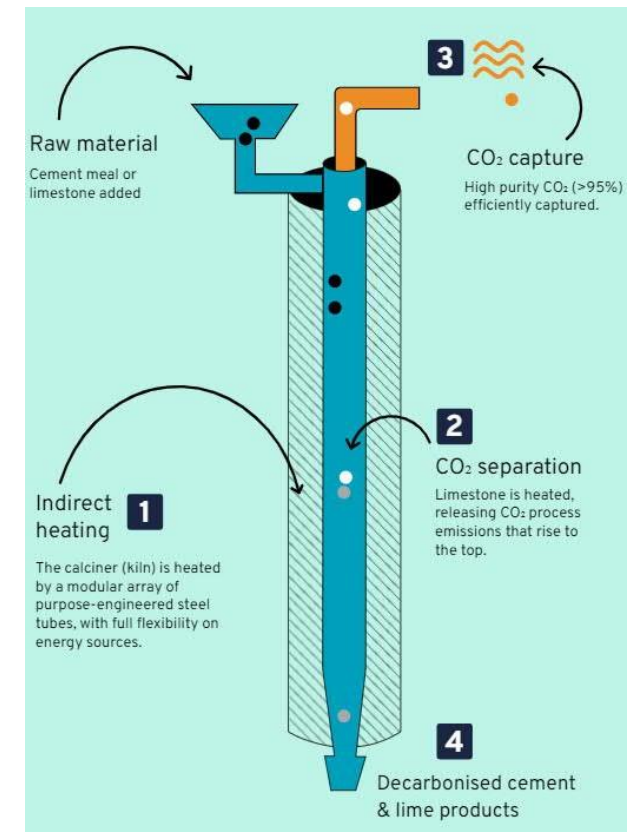
Specific carbon capture process for cement production

### Direct CO<sub>2</sub>-Separation for Cement: LEILAC 1

- > unavoidable CO<sub>2</sub> emitted from the limestone
- > indirect heating of the limestone in a special steel reactor
- > Direct separation of the pure CO<sub>2</sub> released by the limestone
- > No additional separation process needed

Source:

[Leilac 1 \(Low Emissions Intensity Lime And Cement\)](#)



# SICK Solutions for the CCUS Value Chain

SICK experiences with the Leilac 1 project

## Carbon capture at a cement plant – LEILAC1 Pilot

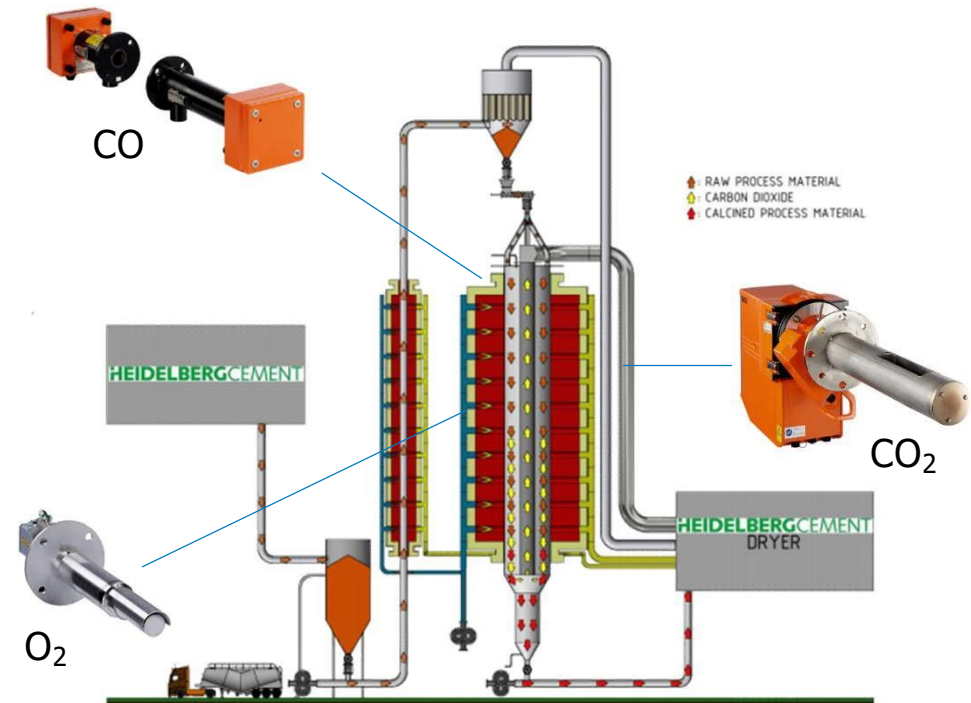
> Carbon Capture pilot plant with CALIX Europe and HeidelbergCement in Belgium

> **Provided SICK Solutions:**

- Process gas analyzer : separated CO<sub>2</sub> concentration with GM35
- Combustion control: with GM901 (CO) and Zirkor100 (O<sub>2</sub>)

**Link to Leilac:**

[Leilac\\_1 \(Low Emissions Intensity Lime And Cement\)](#)



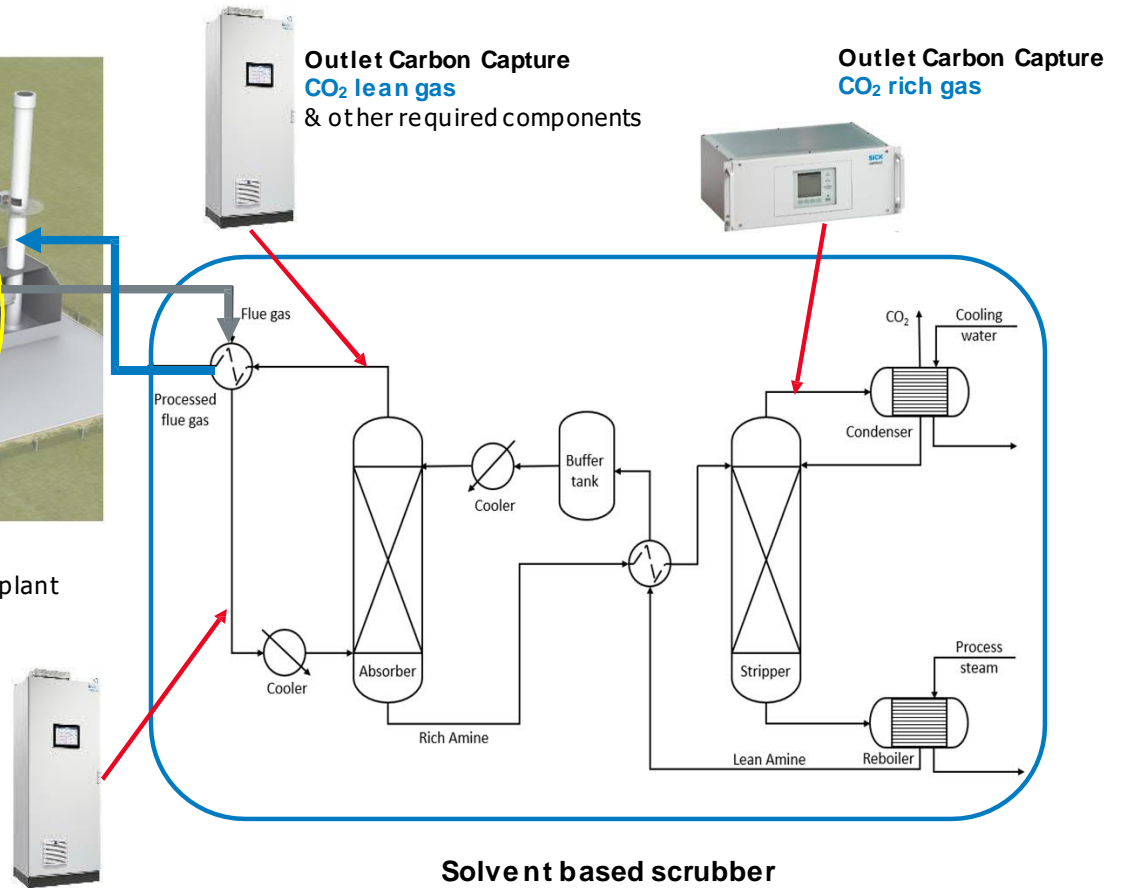
# SICK Solutions for the CCUS Value Chain

Measurements for post-combustion carbon capture



**Part of the flue gas treatment**, can be retrofitted to each industrial plant  
 Example with solvent based scrubber

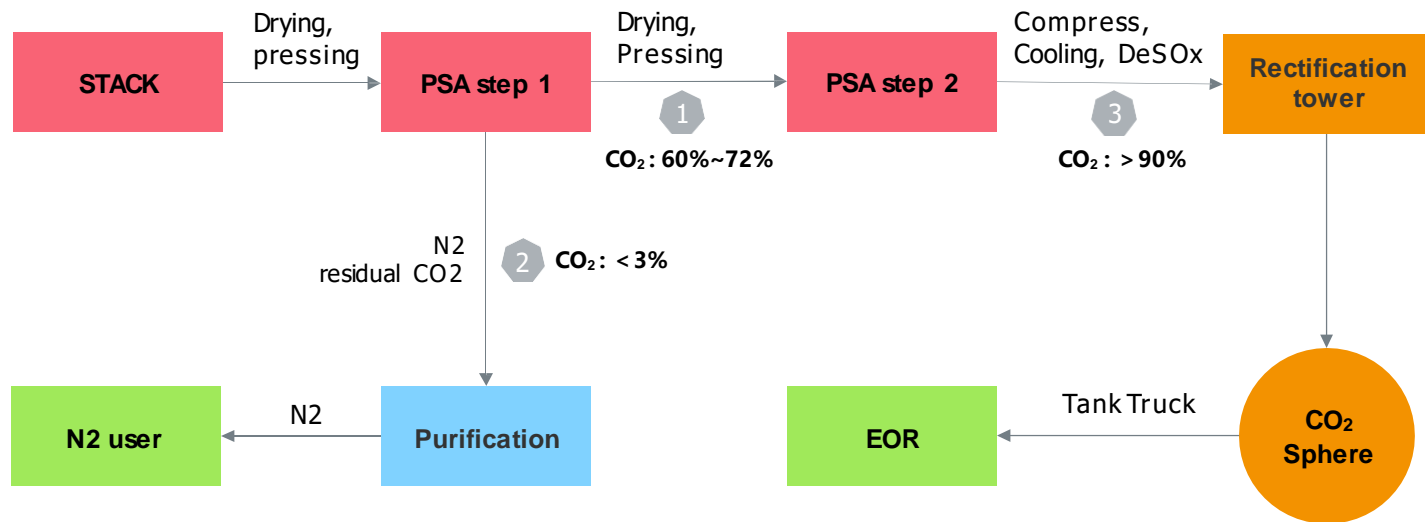
**Inlet Carbon Capture** Raw gas after the standard FGT  
 CO<sub>2</sub> & other required components like SO<sub>2</sub>, dust...



# SICK Solutions for the CCUS Value Chain

Example with a PSA capture process

CO<sub>2</sub> & N<sub>2</sub> Capture at a Coal Fired Power Plant  
Using Pressure Swing Absorption process



### 3 measuring points:

- 1 The bottom outlet of PSA step 1 , CO<sub>2</sub> 60%~72% (**SIDOR CO2 60%~100%**), pressure 21kpa, pressure stable
- 2 The top outlet of PSA step 1 , residual CO<sub>2</sub> < 3% (**SIDOR CO2 0%~5%**), pressure 0.78MPa, pressure stable
- 3 The bottom outlet of PSA step 2 , CO<sub>2</sub> > 90% (**S710 UNOR CO2 80%~100%**), pressure 2.27kpa, pressure stable





# SICK Solutions for the CCUS Value Chain

## Summary

### **CCUS is a key element for mitigating climate change and to reach the high CO<sub>2</sub>-emission reduction targets**

- > **CO<sub>2</sub> separation** for the production of **fossil-based energie**
- > **Reduction of unavoidable CO<sub>2</sub>** from hard-to-abate industries (Cement, steel, petrochemical plants...).
- > **Clean gas production**: natural gas production, blue hydrogen / Ammonia production with CCUS

### **Continuous measuring technologies to control the complete CCUS ecosystem**

- > **Efficiency** of CO<sub>2</sub>-capture processes
- > **Quality** of the gas matrix
- > **Flow** metering

### **Challenges and diversity of applications**

- > **Unclear Specification** for CO<sub>2</sub> and impurities
- > **Diversity of applications** along the CCUS value chain

# Carbon Capture, Utilization and Storage

Dedicated brochures and tools for CCUS

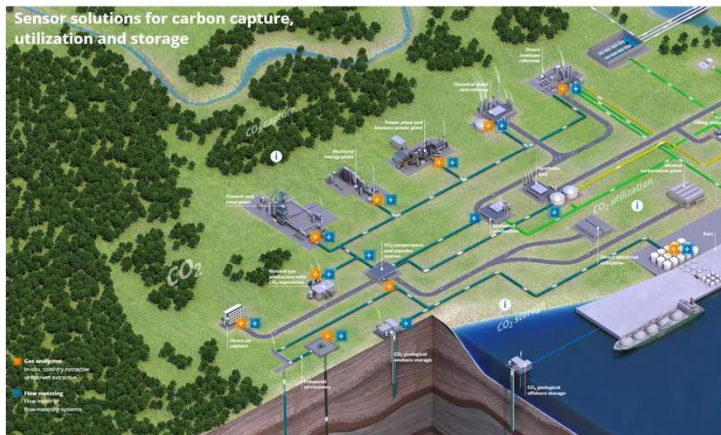


Useful links:

[SICK Solutions for Carbon Capture Utilization and Storage](#)

[Special Information about CO<sub>2</sub> Flow Measurement](#)

[Special information CCUS](#)



# Carbon Capture, Utilization and Storage

For further information



Link to the SICK CCUS website:

[www.sick.com/ccus](http://www.sick.com/ccus)

## Aurélie Moll

Head of Industry Group Energy & CCUS



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Mobile: +49 172 76 68 601  
E-Mail: [aurelie.moll@sick.de](mailto:aurelie.moll@sick.de)  
Website: [www.sick.com](http://www.sick.com)  
[linkedin.com/in/aurelie-moll/](https://www.linkedin.com/in/aurelie-moll/)

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## Carbon capture, utilization and storage (CCUS)

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**CARBON CAPTURE, UTILIZATION AND STORAGE**  
Special information

The level of carbon dioxide (CO<sub>2</sub>) released into the atmosphere has increased significantly since the beginning of the industrial era. Unless we do something to reduce the amount of CO<sub>2</sub> entering the atmosphere, the world will experience the effects of climate change. Carbon capture, storage and utilization will be an essential part of the decarbonization process for mitigating climate change and could be a path to a low-carbon future. Carbon capture is a technology approach that can remove up to 90% of the carbon dioxide (CO<sub>2</sub>) emissions and store it safely in a geological storage site.

# Measurement of emissions from CCUS

Rod Robinson, [rod.robinson@npl.co.uk](mailto:rod.robinson@npl.co.uk)

Principal Scientist, Emissions and  
Atmospheric Metrology Group, NPL

WP2 Lead



# WP2 Metrological support for the measurement and reporting of CO<sub>2</sub> emissions to air

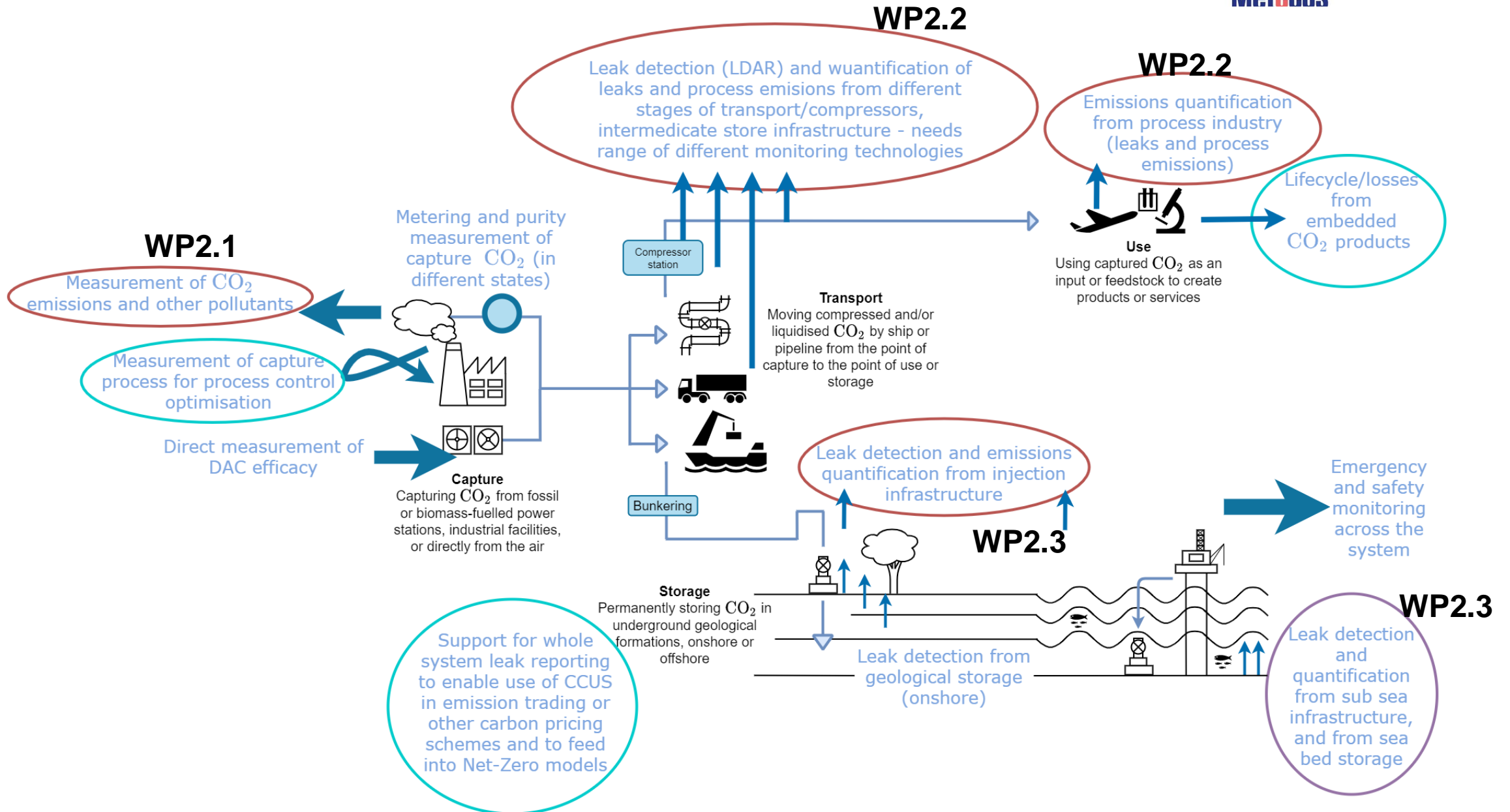


## • Three tasks

- Task 2.1 will develop novel methods to determine CO<sub>2</sub> and other emissions to the atmosphere from carbon capture processes. (**NPL, Force**, PTB)
- Task 2.2 will develop the metrological capability needed for the measurement and quantification of emissions of CO<sub>2</sub> from CCUS equipment and infrastructure. (**NOVA, NPL, FORCE**, SINTEF, GERG)
- Task 2.3 will assess the potential approaches needed to enable the detection and quantification of emissions of CO<sub>2</sub> into the environment from geological storage. (**PTB, NPL, VTT**, GERG, NOVA)

D3	Good practice guide for the measurement of nitrosamines in post-combustion flue gas in order to enable the direct determination of emissions of CO <sub>2</sub> and to address the measurement of air pollutants resulting from the capture process, such as degradation products from capture solvents	Good practice guide	NPL, Force	Jul 2025 (M34)
D4	Report on the options for the measurement and reporting of emissions to air from different stages of the CCUS process and the performance and capabilities of techniques to monitor emissions into the environment through carbon capture processes, infrastructure (leaks), or geological storage	Report	PTB, VTT, NPL, NOVA, GERG	Sep 2025 (M36)

# Monitoring the CCUS System



# Measurement of emissions of CO<sub>2</sub>

- We can assume the main sources will be similar in a CCUS system as in the gas system
  - Fugitive leaks from components/seals/etc
    - LDAR programmes, optical gas imaging (OGI)
  - Process related vents/releases
    - Lower emission designs, OGI
  - Maintenance and repair operations
    - Engineering, design
- Measurement requirements
  - LDAR – leak detection and repair
  - Source level quantification
  - Site/area scale quantification
- CCUS specific issues
  - Requirements very challenging to meet CCS Directive
  - Ambient background levels of CO<sub>2</sub>
  - Dispersion characteristics
  - Phase of contained fluid
  - Similar techniques to methane are available





# Development of test benches to determine the detection limit of CO<sub>2</sub> sensitive gas imaging cameras

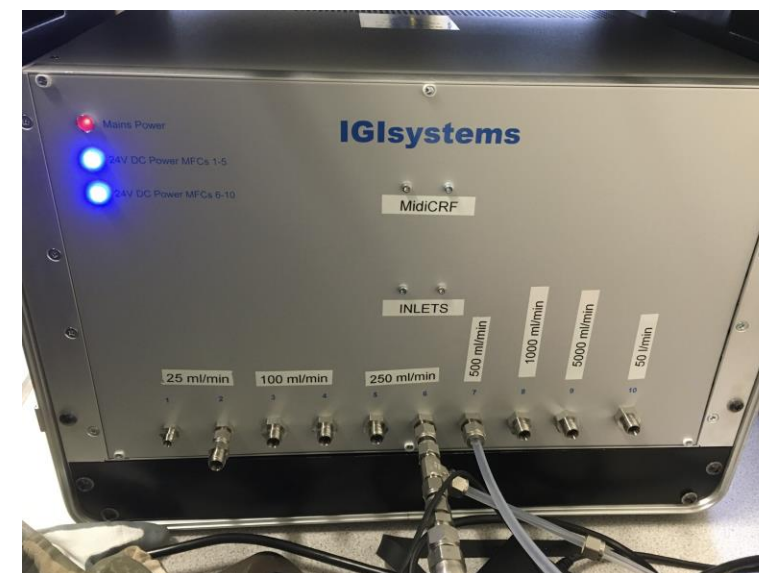
Z. Khan, J. Helmore





# Adaption of controlled release and test facilities for CO<sub>2</sub>

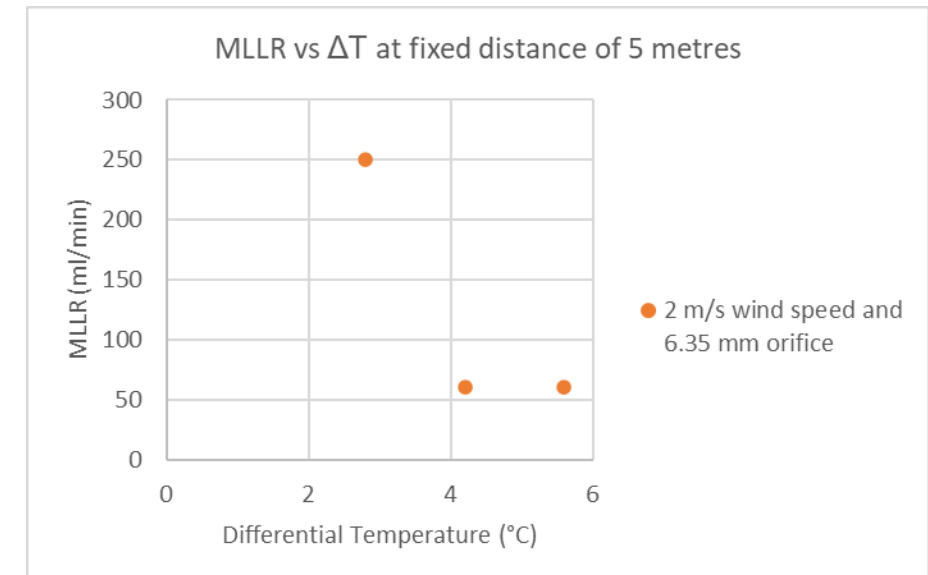
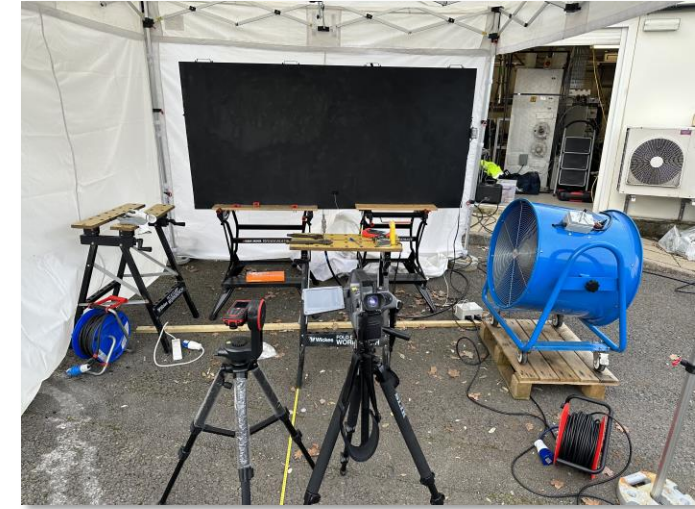
- NPL currently operates several systems which allow for the creation of controlled emissions between 5 ml/min and 500 l/min (0.2 g/h – 20 kg/h) for methane (natural gas). Expanded uncertainties are typically  $\leq 7.5\%$ .
- Within the MetCCUS project activities, release facilities were calibrated for accurate delivery of CO<sub>2</sub> emissions, with rates between 5 ml/min and 50 l/min (0.6 g/h to 5.9 kg/h). Expanded uncertainties achieved  $\leq 3\%$ .



# Assessing the detection limits of CO<sub>2</sub> gas

## imaging cameras

- Adaption of test protocols used for assessing the performance of hydrocarbon sensitive gas imaging cameras to those sensitive to CO<sub>2</sub> under controlled and uncontrolled environmental conditions.
- Assessing detection limits as a function of range, differential temperature and windspeed.
- If  $\Delta T$  is sufficient ( $>4$  °C) leaks of  $\sim 60$  ml/min ( $\sim 7$  g/h) can be consistently detected.



# Adaption of test facilities for CO<sub>2</sub>

- Modification of existing test benches used for methane (natural gas) for use with CO<sub>2</sub>.
- Adaption of test protocols used for assessing the performance of hydrocarbon sensitive gas imaging cameras to those sensitive to CO<sub>2</sub>.
- As with hydrocarbon sensitive gas imagers detection will be dependent of  $\Delta T$  conditions in the field, which may not be possible to accurately determine, and relies heavily on operator experience.

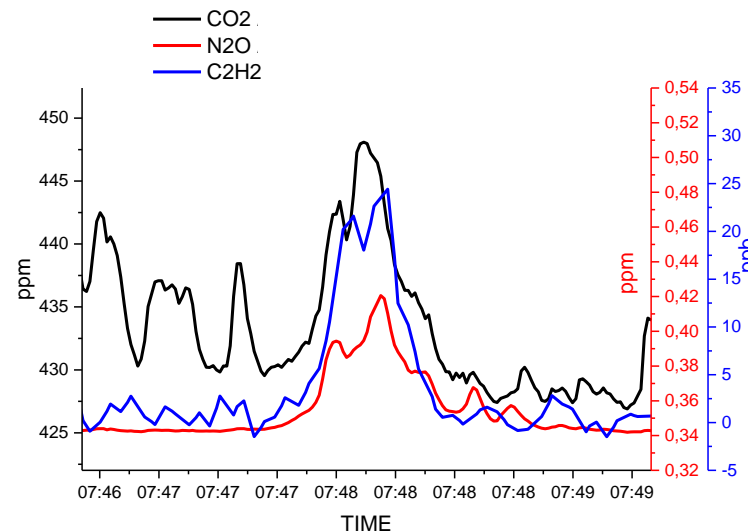
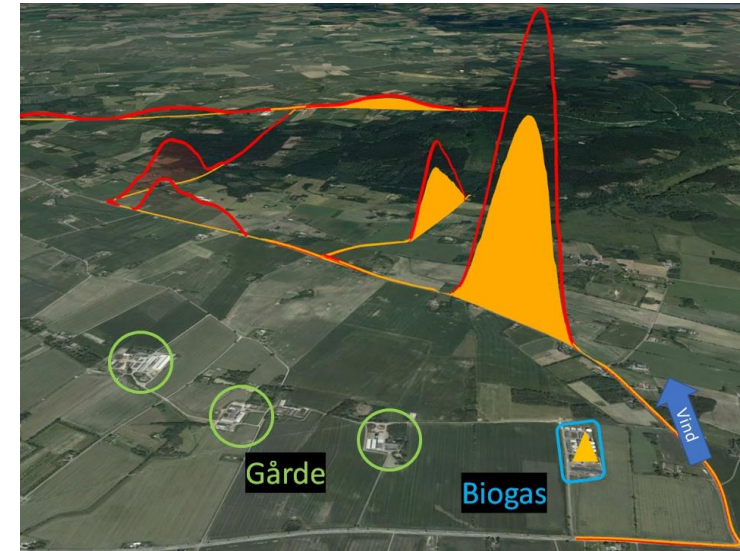
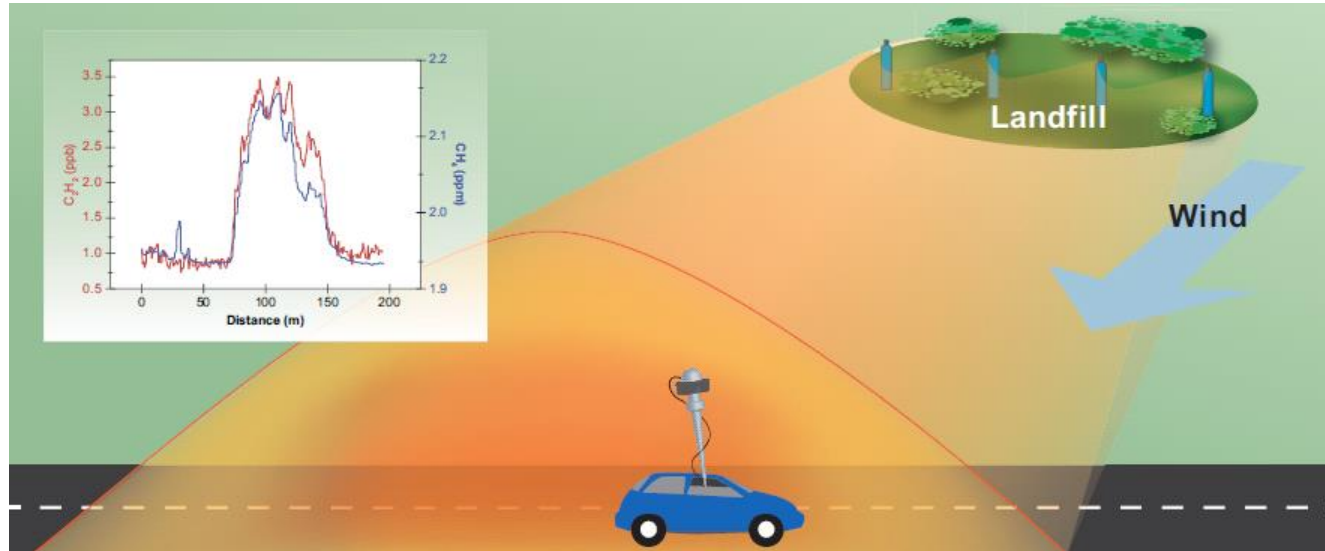


# Future work with respect to CO<sub>2</sub>

- Future work will look to increase the range of our capability in terms of controlled CO<sub>2</sub> emissions, to enable testing of DIAL and other methods.
- There are significant challenges with handling CO<sub>2</sub> in larger quantities and delivering higher flow rates due to the energy required to vaporise the fluid.
- Development and testing of a high flow sampling method for quantifying CO<sub>2</sub> emissions.



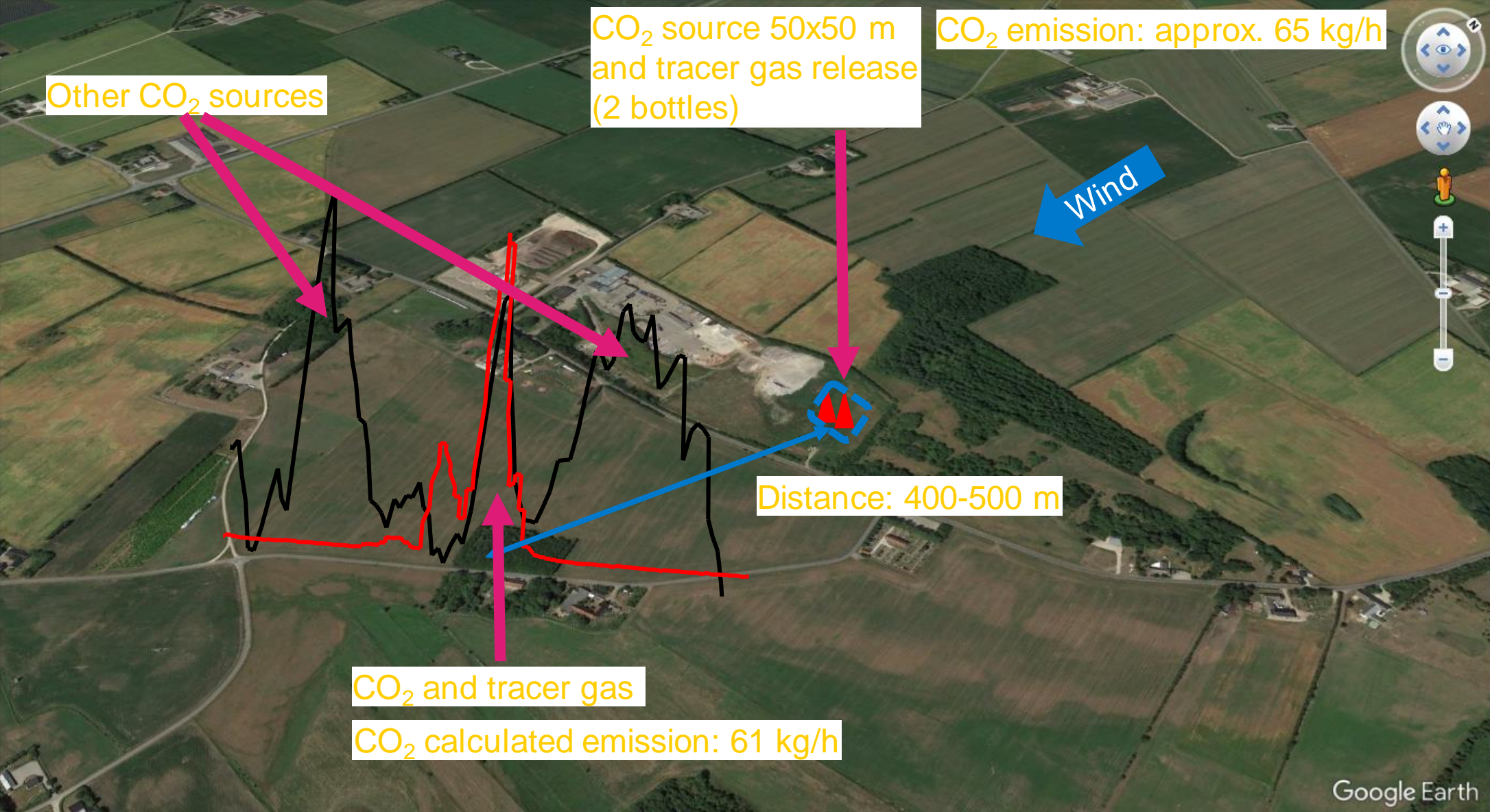
# Tracer correlation method



**CO<sub>2</sub> emission:**  
 Size (m<sup>2</sup>)  
 Strength (g/s)

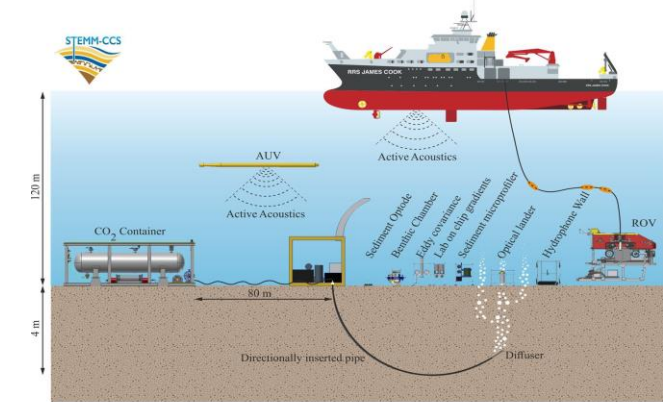
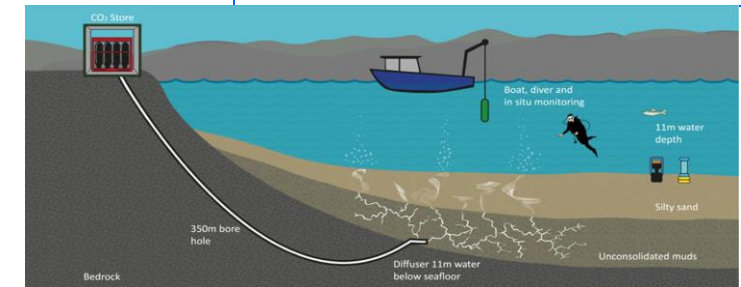
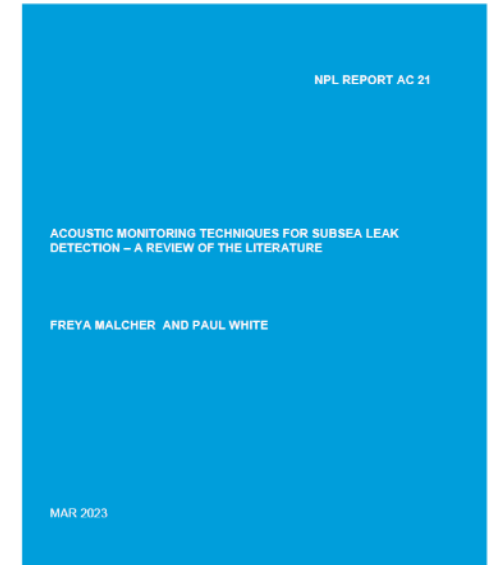
Distance needed/possible  
 Choice of tracer gas

# Tracer correlation method for diffuse CO<sub>2</sub> emission



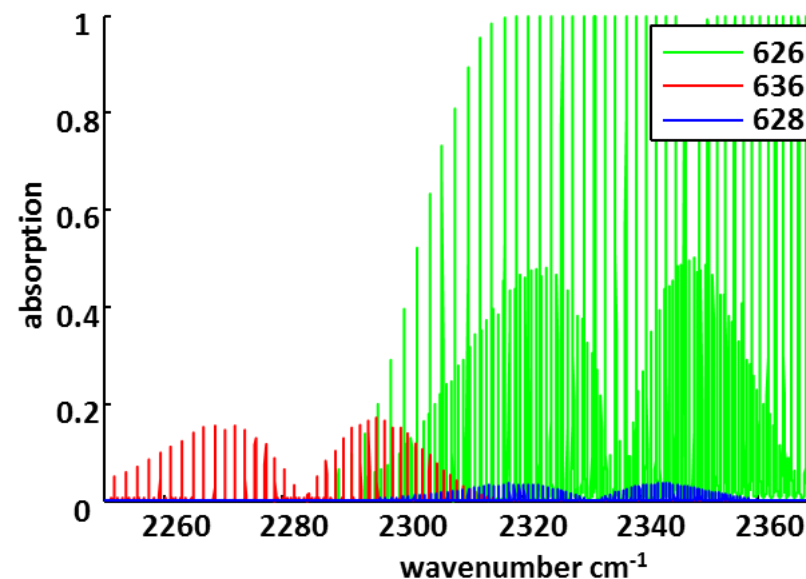
# MetCCUS, Subsea leakage from storage

- **NPL review of acoustic techniques**
- **NPL report AC21 published**
- reviews physics of sound-bubble interaction, active and passive techniques, and existing offshore projects
- **Active and passive acoustic techniques**
- passive uses only hydrophones to listen for leaks
- active insonifies target and detects sound scattered by bubbles
- **Review of existing in-situ offshore projects**
- ECO2 (2011-2015)
- QICS (2012)
- STEMMS-CCS (2016-2020)
- **Next steps and knowledge gaps**
- re-evaluation of existing datasets using new models
- better understanding of depth dependence
- Greensands new active acoustics project (Denmark)

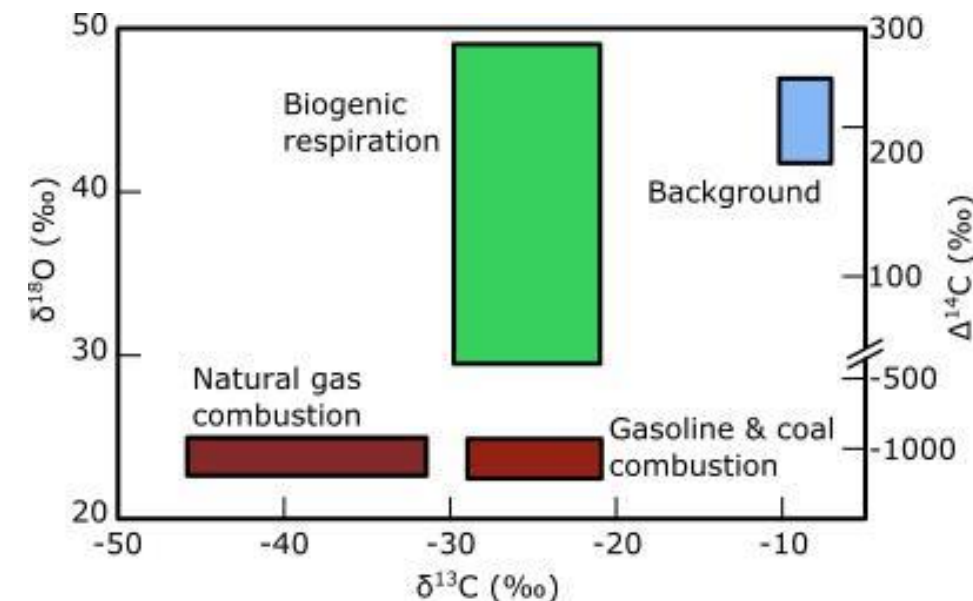


# Analyser for leak detection from CCUS

- Stored CO<sub>2</sub> has a **distinctive isotopic composition** which is different from atmospheric CO<sub>2</sub>
- **Can be used as a tracer of leaks**
- Compact device based on mid-infrared laser sources will be used for **on-line monitoring**
- Adapt existing instrument for **in situ leak detection**, e.g., by adding a multi-pass cell
- Investigate limitations and how it can be used to **quantify** leaks



Source identification diagram for CO<sub>2</sub>







# Monitoring emissions from the capture process

Haydn Baros, Richard Harvey, Hannah Cheales,  
Chris Dimopoulos, Rod Robinson

(Joint activities – MetCCUS and UK EA project)

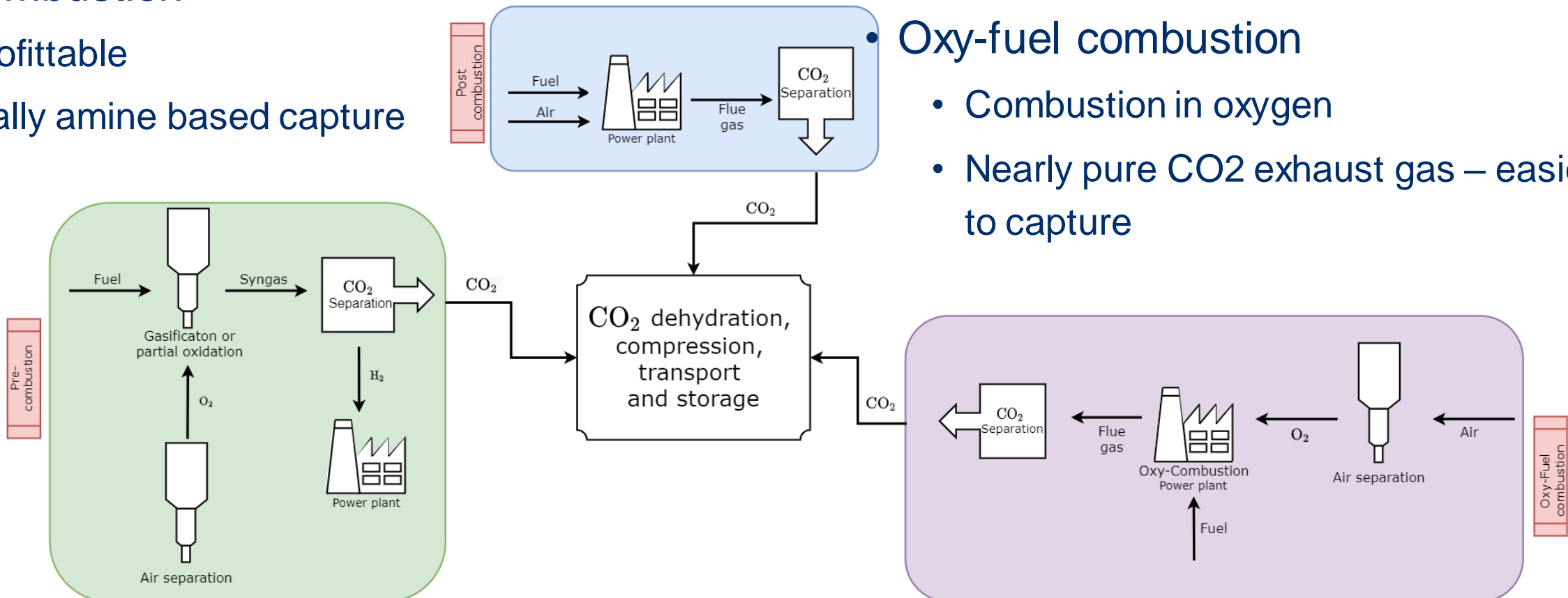
# Carbon capture

- There are three main approaches to capture CO<sub>2</sub> from combustion processes
- Post combustion
  - Retrofittable
  - Usually amine based capture
  -

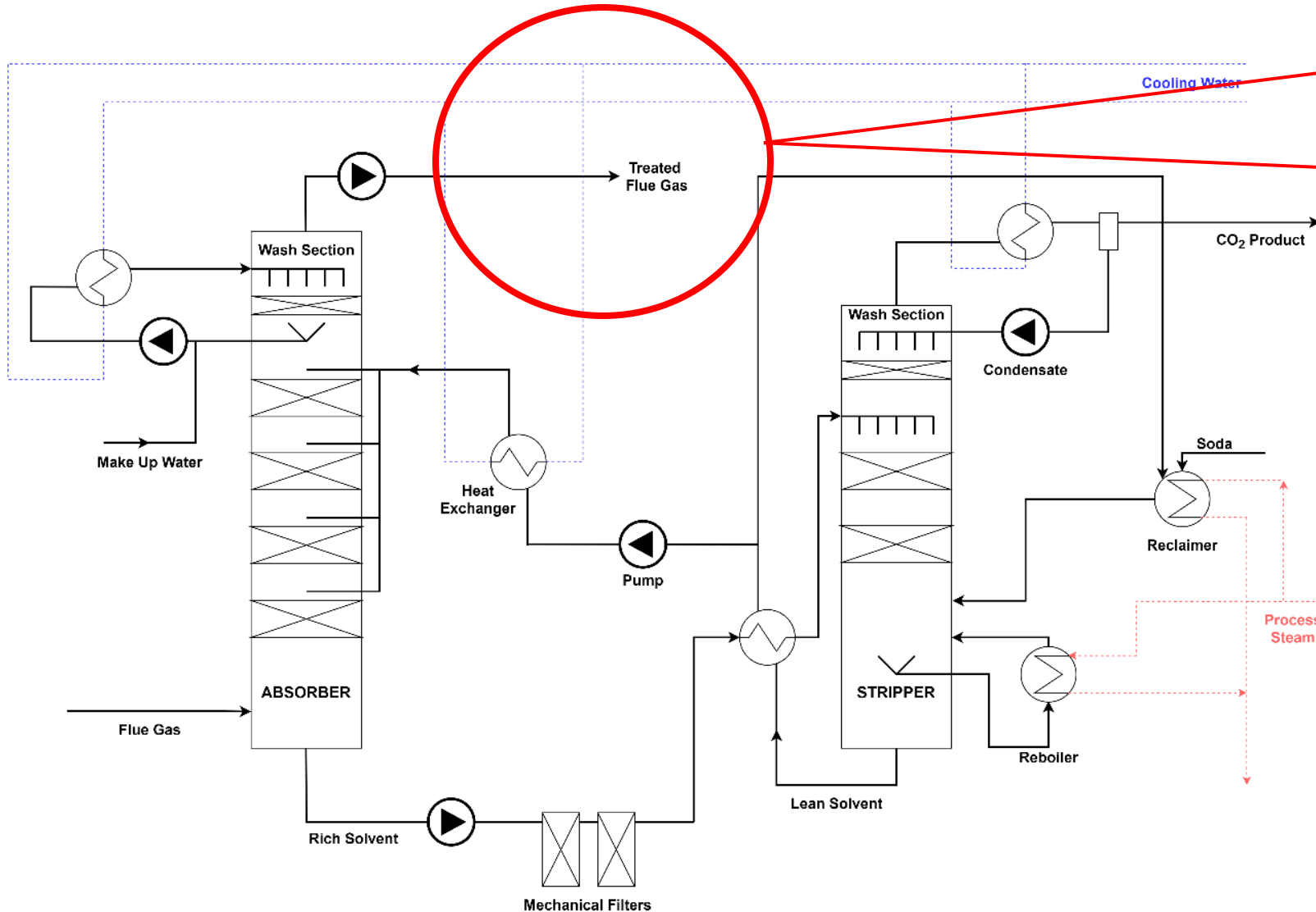
- Pre-combustion carbon capture
  - Gasification of fossil fuel,
  - Generally linked to hydrogen production

## • Oxy-fuel combustion

- Combustion in oxygen
- Nearly pure CO<sub>2</sub> exhaust gas – easier to capture



# Post Combustion Capture



Flue gas conditions,  
Low flow rate  
Low CO<sub>2</sub>  
High water content  
Low temperature  
Effects of NO<sub>x</sub>

- Direct measurement of CO<sub>2</sub>, post capture

  - Determination of capture efficiency from mass balance involves subtraction of two large numbers so uncertainty is high

  - Direct measurement – has potential for lower uncertainty – need sensitive analyser – ambient levels, with sampling system able to handle stack conditions, dilution probe

- Effect of post capture gas matrix on regulated pollutant monitoring

  - Reference methods not validated for low CO<sub>2</sub>, high water vapour conditions, droplets

  - Post capture is a new class of emission (reference levels different)

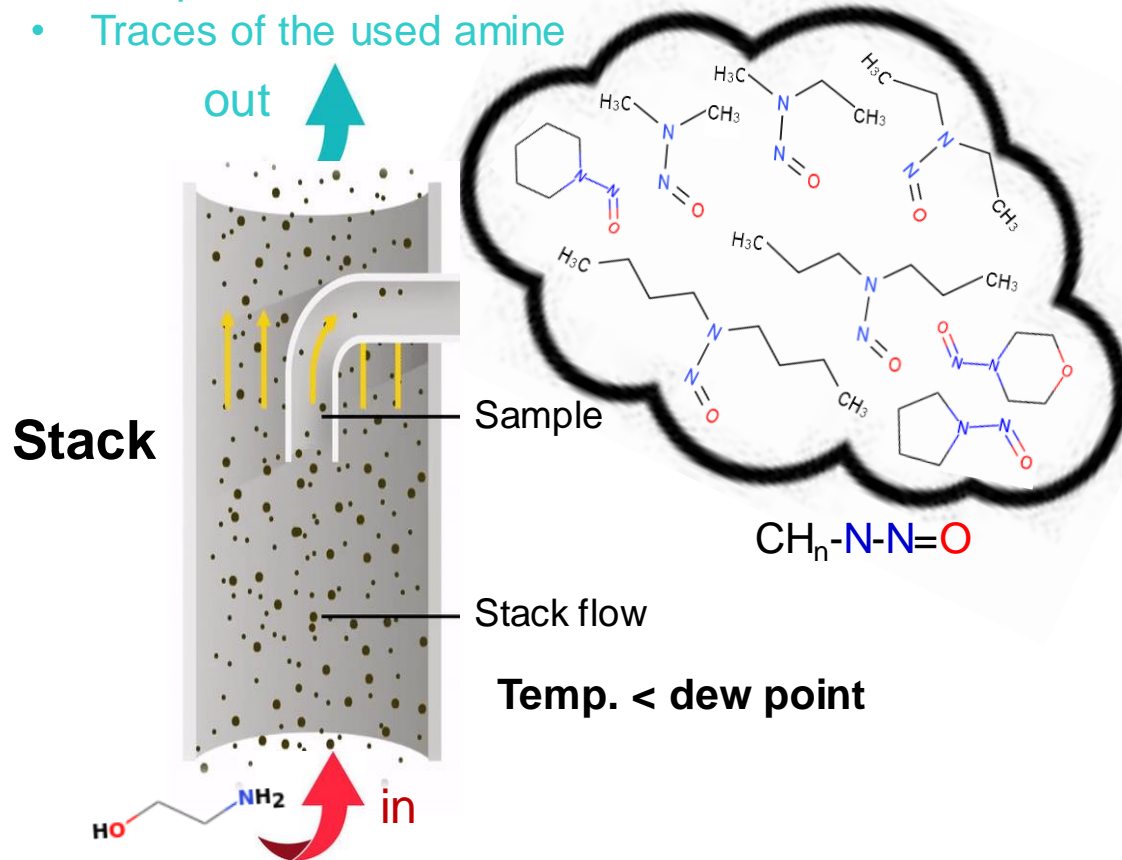
- Dispersion characteristics different

- New pollutants

  - Amines and break down products
  - SO<sub>3</sub>

# CO<sub>2</sub> Capture Emissions Monitoring: Proposal of nitrosamine's sampling methods

- Exit gas (CO<sub>2</sub>-depleted) + water droplets
- Complex amines & nitrosamines
- Traces of the used amine



- Exhaust gas (N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, CO, etc.)
- Sorbent solution (simple amines like MEA @ 30%)

## Metrological challenges

- Complex transport (gas + water droplets)
- Volatility covering 5 orders of magnitude
- Solubility not well known
- Oily and sticky
- Reactive with several substances/surfaces
- Formation of new NNS within the sample

## Environmental and health challenges

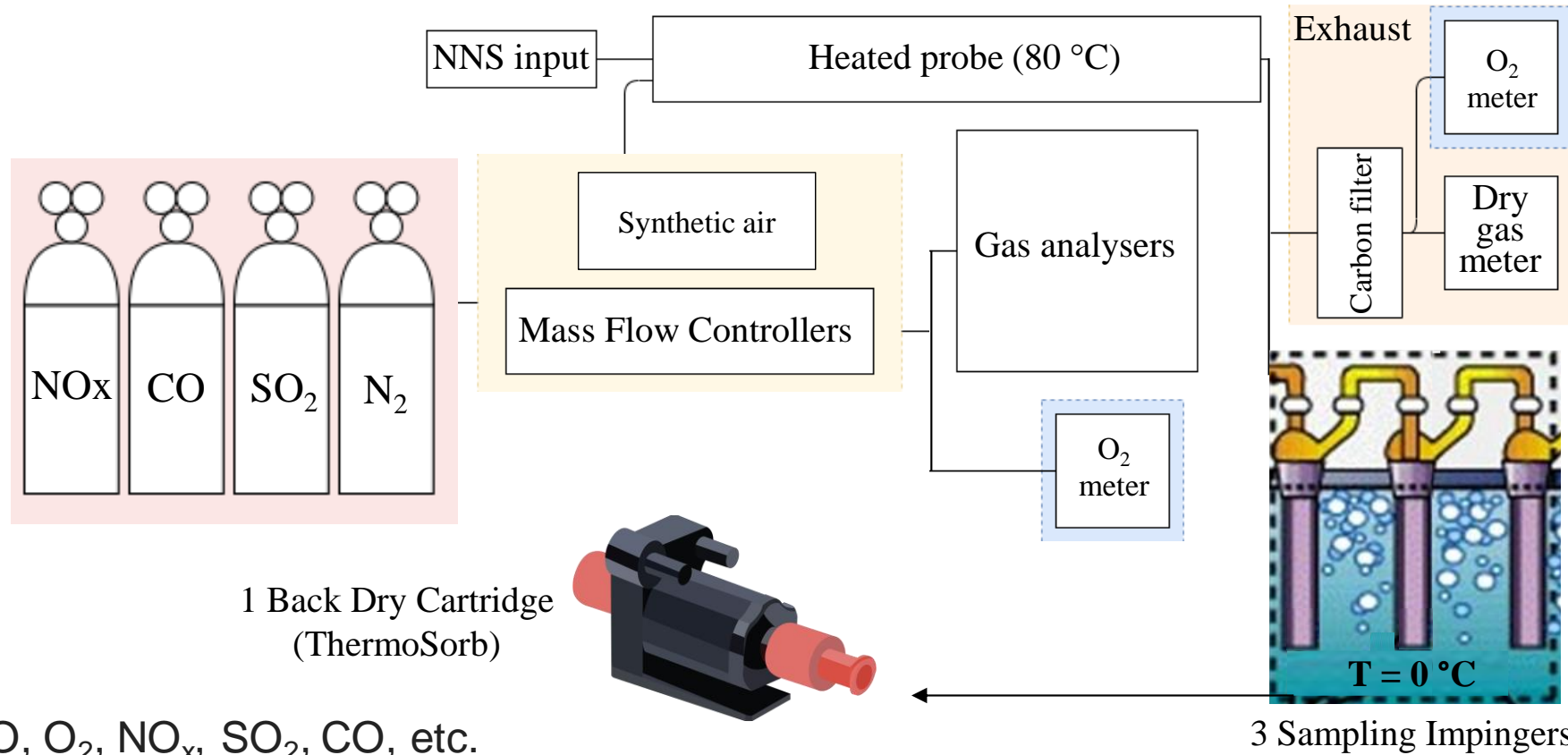
- Corrosive
- Carcinogenic
- Mutagenic
- Teratogenic



## Testing

- Scaled down stack simulator at NPL
- Controlled conditions (Lab)
- Wet and dry isokinetic sampling
- Stack testing (CCUS post combustion plant)

# Test bench developed for nitrosamine/amine sampling testing

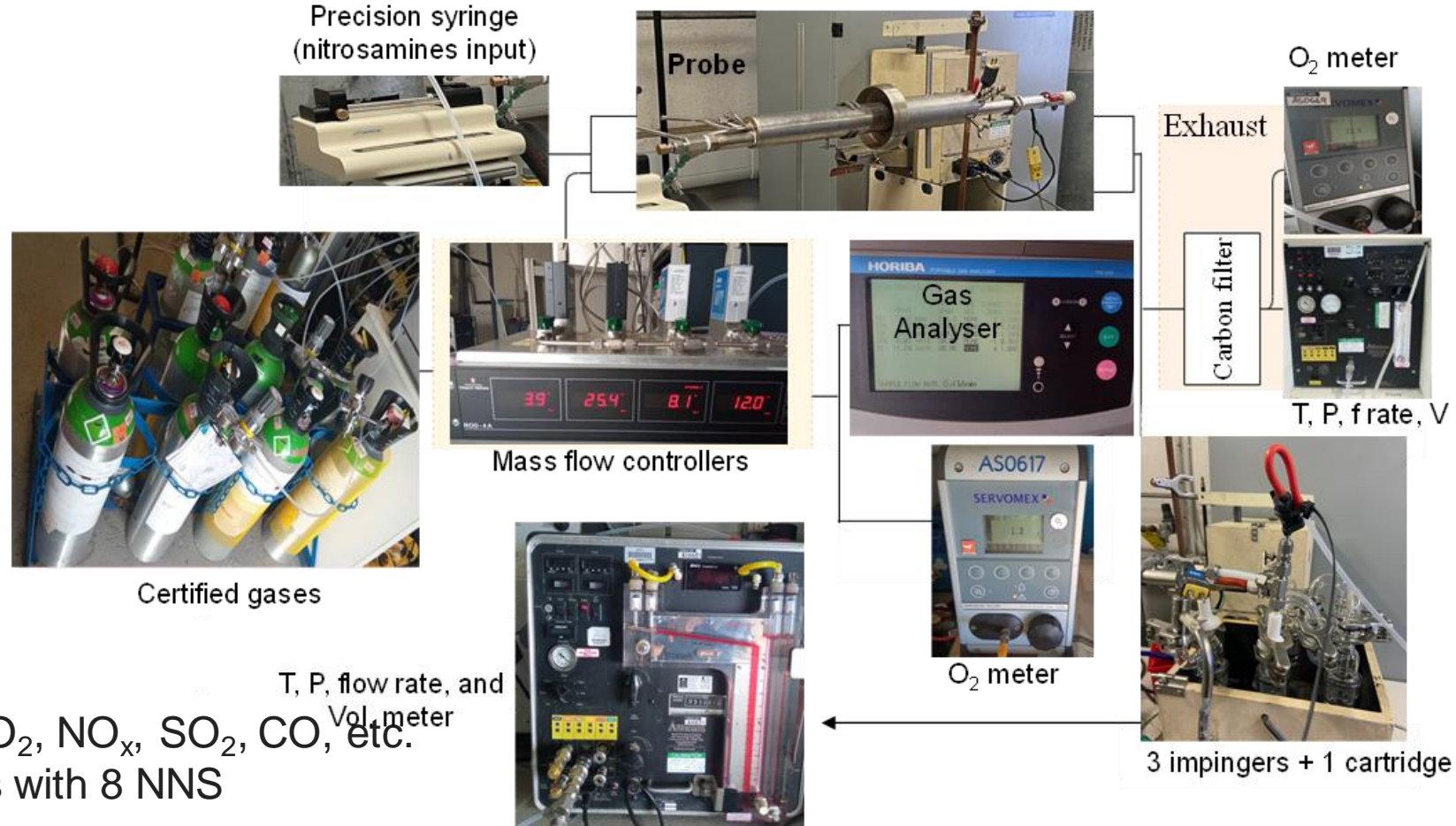


Gas matrix:  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{NO}_x$ ,  $\text{SO}_2$ ,  $\text{CO}$ , etc.  
Experimental tests with 8 NNS

Liquid sampling method (impingers 1 M  $\text{H}_3\text{NSO}_3$ )  
Dry sampling method (Thermo-Sorb cartridges)

Samples measured by GM-TEA (Muller Lab.)

# Test bench developed for nitrosamine/amine sampling testing



Gas matrix: H<sub>2</sub>O, O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, CO, etc.

Experimental tests with 8 NNS

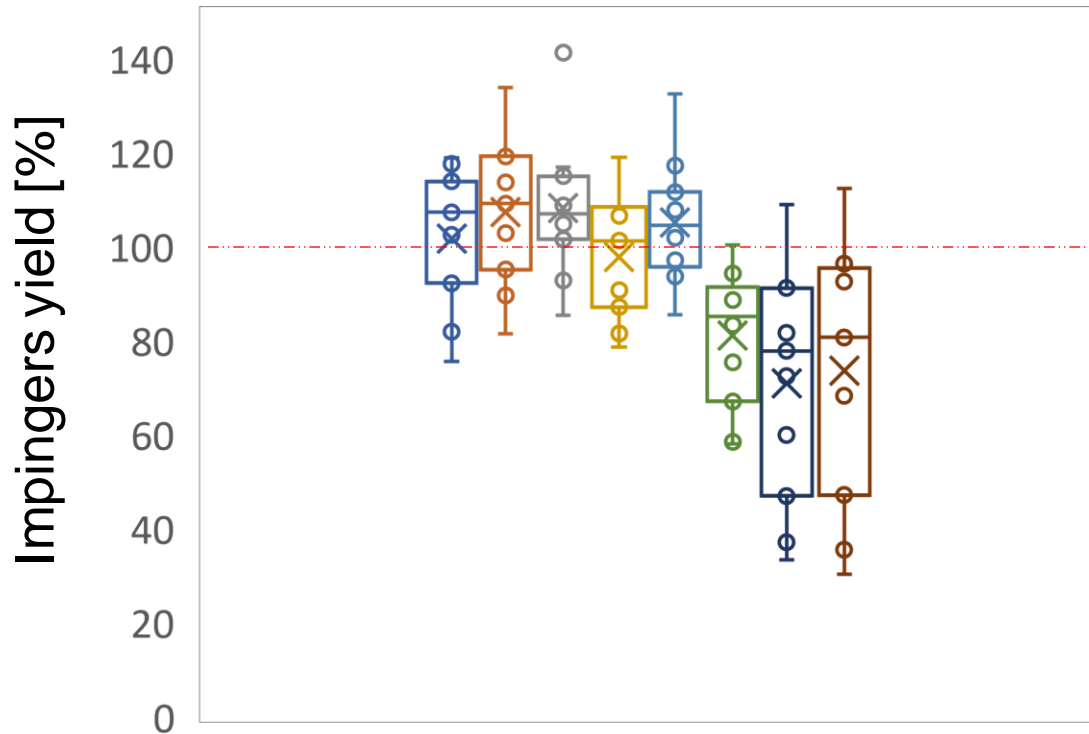
Liquid sampling method (impingers 1 M H<sub>3</sub>NSO<sub>3</sub>)

Dry sampling method (Thermo-Sorb cartridges)

Samples measured by GM-TEA (Muller Lab.)

# Results: Liquid sampling method

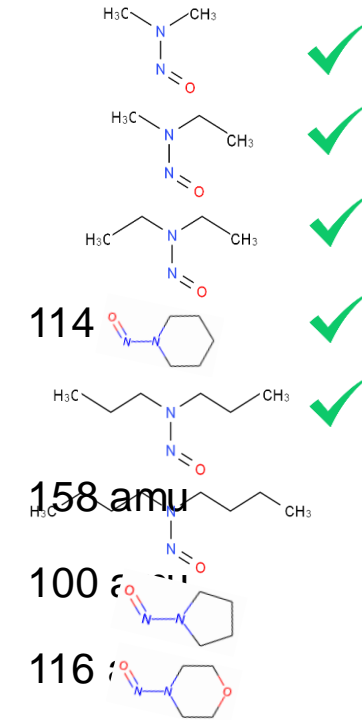
## Criterion 1: Total nitrosamine's sampling yield [%]



3 impingers combined, n=11

NNS VP@20°C m. mass

NDMA	0.4 kPa	74 amu
NMEA	0.15 kPa	88 amu
NDEA	0.11 kPa	102 amu
NPIP	0.012 kPa	114
NDPA	0.011 kPa	130 amu
NDBA	0.006 kPa	158 amu
NPYR	0.005 kPa	100
NMOR	0.005 kPa	116



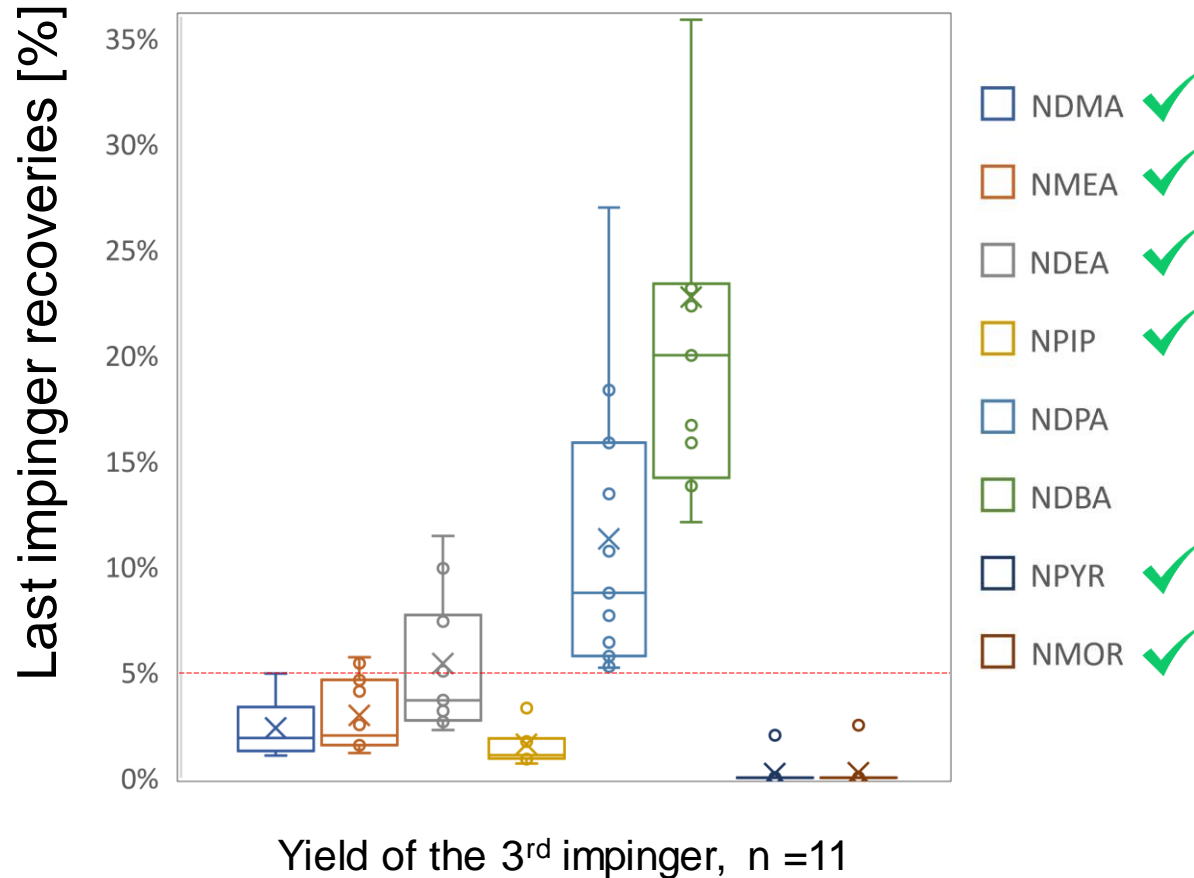
Each total (100%) is defined as the addition of the mass collected in the three impingers

The three nitrosamines with lower volatility were partially trapped within the test system (yield < 80%)



# Results: Liquid sampling method

## Criterion 2: Nitrosamine's sampling yield of the last impingers (# 3)



Nitrosamine	3 <sup>rd</sup> impinger yield
NDMA	2 ± 1 %
NMEA	3 ± 2 %
NDEA	5 ± 3 %
NPIP	2 ± 1 %
<b>NDPA</b>	<b>11 ± 7 %</b>
<b>NDBA</b>	<b>23 ± 12 %</b>
NPYR	0.2 ± 0.6 %
NMOR	0.2 ± 0.7 %

The check is passed if last impinger < 5%.

Performance standard for manual stack emission monitoring. Environment Agency. January 2019. V 8.

The two linear nitrosamines with lower volatility were significantly trapped within last impinger

# SUMMARY

- Impingers recoveries range 70 – 110 %, while the total recovery shows analytical overestimation
- Nitrosamines volatilities play a major role in the sampling methods, and its influence is expected in
- PCC processes, stacks dynamics and environmental dispersion
- Ring-type NNS have lower recovery as compared with linear ones with similar volatility
- Cross contamination was observed, and a better probe/impinger cleaning is now applied
- Surfaces conditions affect drastically the impingers recoveries for low volatile NNS
- Repeatability exhibit a large variability
- The “sampling method + analytical measurement” must be considered as semiquantitative
- It is necessary to test with different conditions and concentrations to see if the observed trends holds
- Dry sampling method was discarded since results are largely affected by the required dilution
- Solubility is another key parameter, however available data have large variation



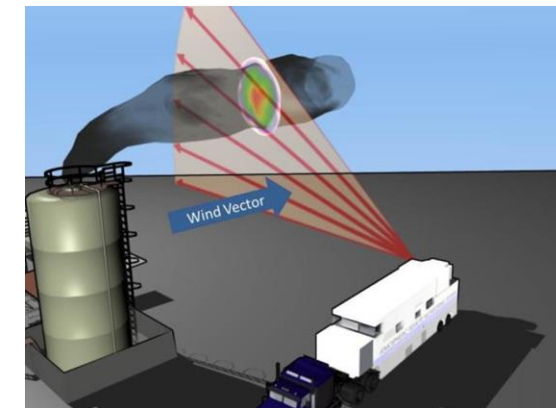
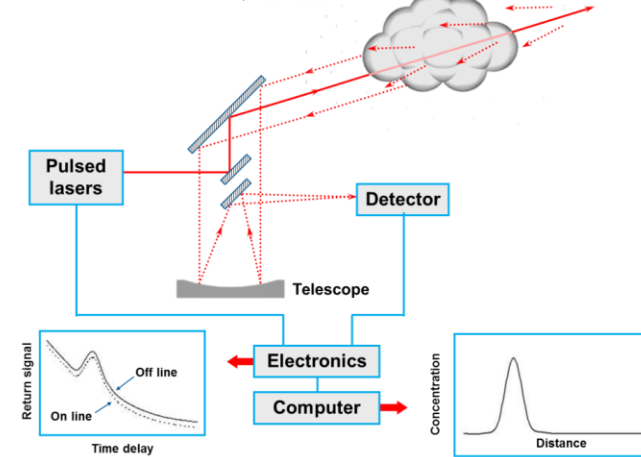
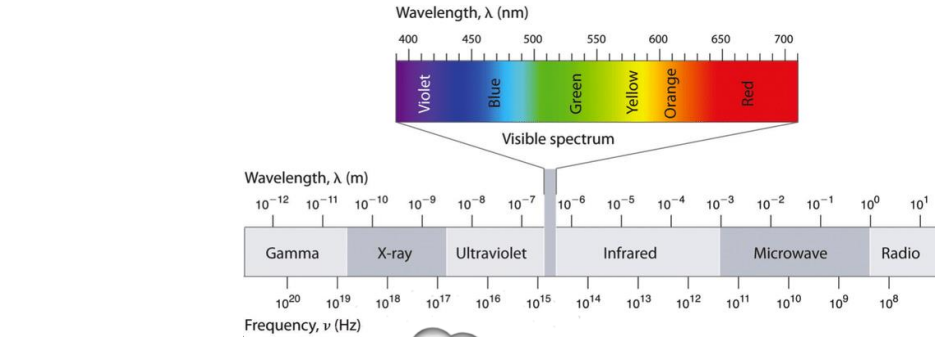
# Monitoring of CO<sub>2</sub> emissions using DIAL

N. Howes, F. Innocenti, A. Finlayson, C. Dimopoulos, T. Gardiner and R. Robinson  
(Decarb project and UK programme)

# DIAL measurement principle

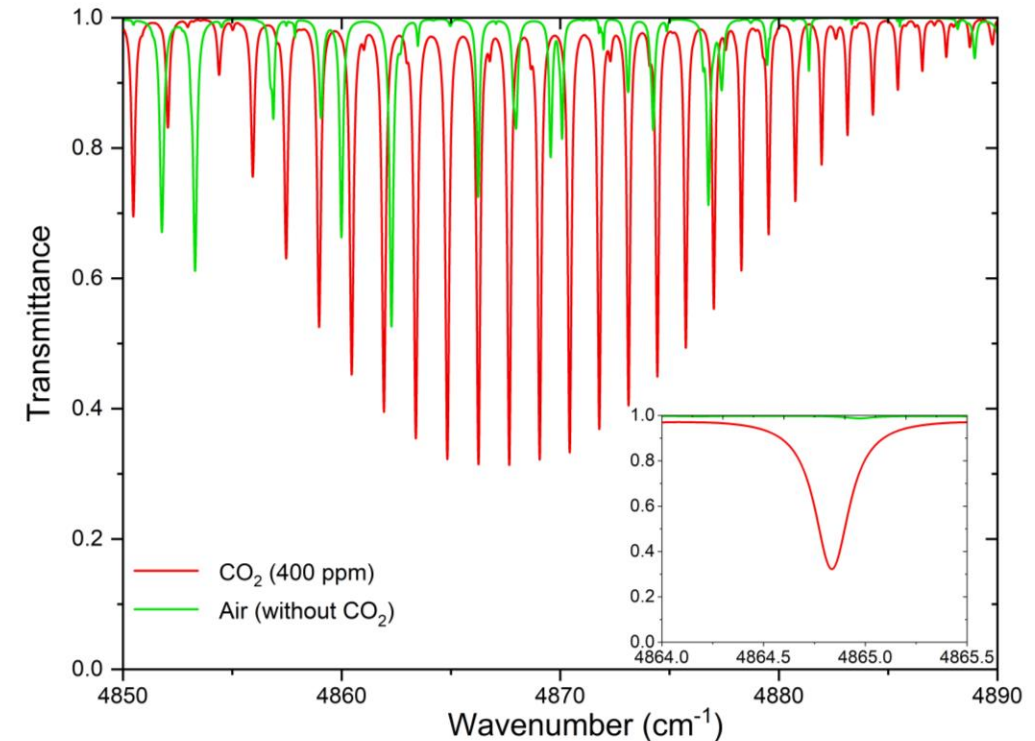
## DIAL - Differential Absorption LIDAR

- ‘LIDAR’ Laser Radar system, which can be targeted on specific gas emissions.
- Gives range-resolved concentration along optical path (Range ~500 metres in IR, ~1 km in UV).
- Spatial resolution < 8 metres.
- Vertical scans enable plume mapping and emission calculation.
- Different wavelengths of light are used to measure different gases, e.g. Near-IR: (3.3-3.4  $\mu\text{m}$ ) - methane, methane, VOCs (including general hydrocarbons)
- Combine integrated concentration with wind field to give quantified emission rate.



# Developing a measurement method for CO<sub>2</sub>

- As CO<sub>2</sub> has a significant atmospheric concentration (~400 ppm, compared to ~2 ppm for methane), careful selection of absorption peaks is required.
- Too strong an absorption peak and the on-resonant energy will be absorbed by the atmosphere. Too weak and detection limit will be extremely high.
- NPL identified a potential region in the 2 μm range where interference from other species is minimal.



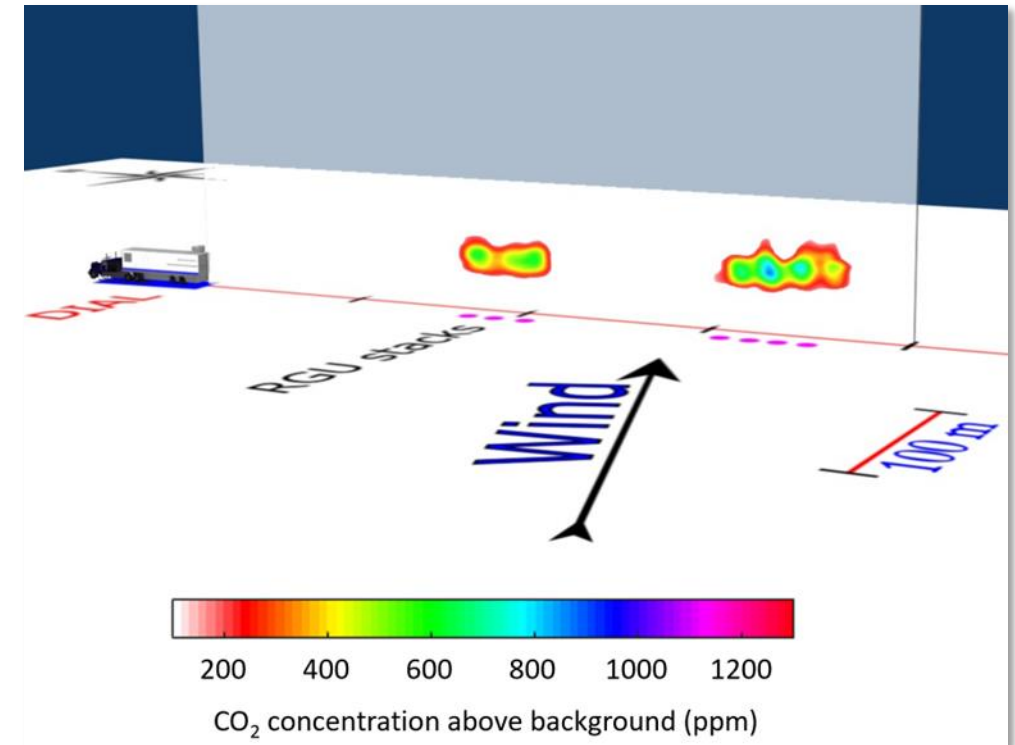
# Validation of CO<sub>2</sub> emissions measurements using DIAL

- In November 2022, NPL carried out a validation exercise at a Liquefied Natural Gas storage and regasification site.
- CO<sub>2</sub> emissions from the regasification plant process were measured simultaneously by NPL teams using DIAL and in-stack monitoring.



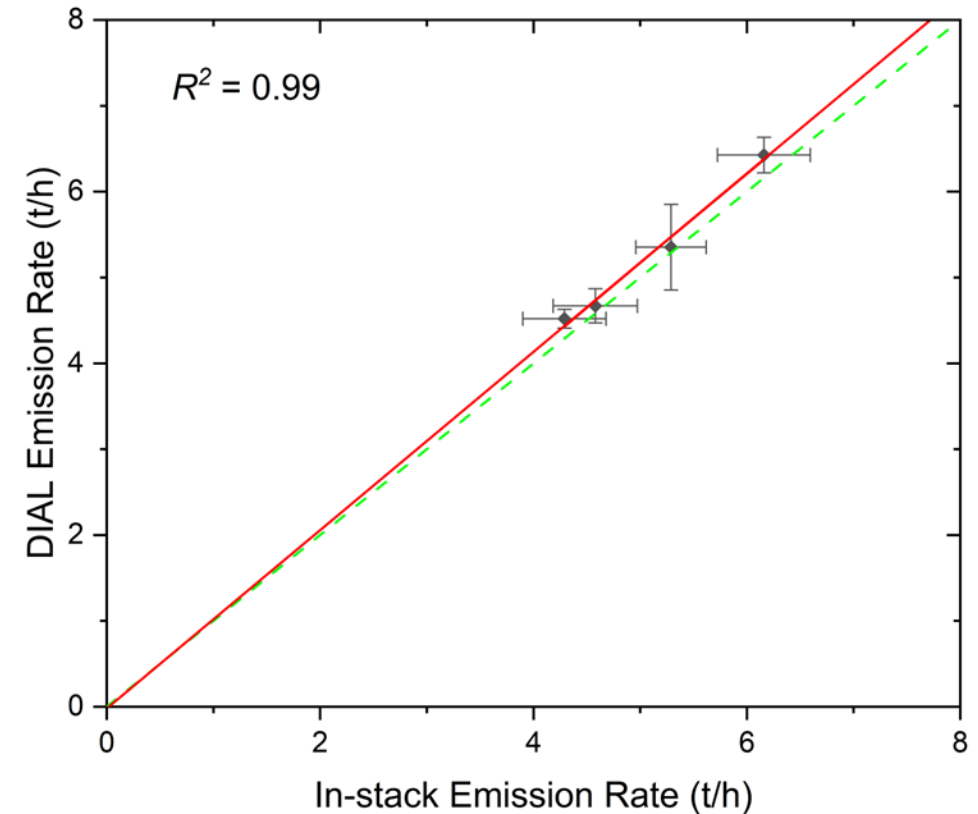
# Validation of CO<sub>2</sub> emissions measurements using DIAL

- During the campaign, CO<sub>2</sub> emissions were measured downwind of seven active stacks simultaneously, as shown below.
- An average emission rate measured from four scans was  $42.2 \pm 5.4$  t/h with the reported uncertainty expanded to provide a 95% level of confidence.
- Using data provided by the operator, it was possible to calculate a comparative emission rate of 40.3 t/h. This value is within the coverage interval of the DIAL measurement.



# Validation of CO<sub>2</sub> emissions measurements using DIAL

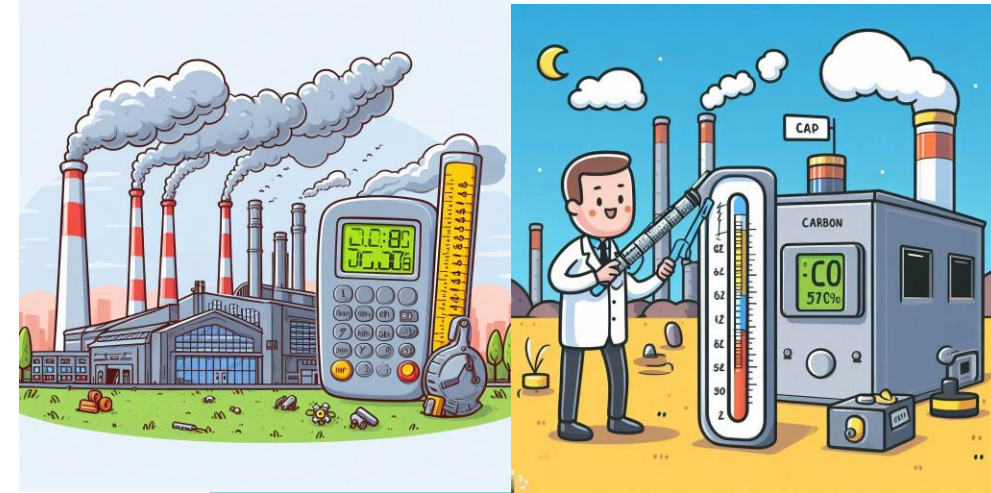
- The results from the DIAL measurements compare well with simultaneous in-stack measurements and suggest that any bias in the DIAL data is likely small.
- Moreover, using the definition outlined in EN 15267-3, a detection limit of 0.12 t/h was estimated for the 2 μm wavelength DIAL data.
- This result is a three orders of magnitude improvement with respect to previous NPL DIAL measurements of CO<sub>2</sub>, made in the 1.5 μm wavelength region.





# Conclusions

- MetCCUS is tackling a number of the issues related to monitoring emissions from CCUS
- Outputs will feed into guidance and standards
- Feedback and inputs from the stakeholder community is important



I asked an AI bot to generate a cartoon of measurement of emissions from industrial carbon capture and storage

METROLOGY  
PARTNERSHIP



**Thank you for your  
attention, any questions?**

[rod.robinson@npl.co.uk](mailto:rod.robinson@npl.co.uk)

The project METCCUS has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

# ▶ CO<sub>2</sub> Specifications for Transport and Thermodynamic Properties

26.10.2023

Online

Roland Span

Sub-Project Leader CO<sub>2</sub> Transport  
EERA JP CCS

Chair of Thermodynamics  
Ruhr-University Bochum



## ▶ **Background**

### ▶ **DG Energy wants to develop a European Transport-Network**

- ▶ Discrimination free access, regulated asset basis, multimodal transport
- ▶ Politics is concerned to see structural disadvantages for regions far from storage sites
- ▶ Industry as driver of the development – situation has changed!
- ▶ Development dynamic, standards / network code urgent!

### ▶ **Need for European standards**

- ▶ So far, specifications for (impurities in) CO<sub>2</sub> are project specific
- ▶ In some countries development of national standards (in Germany DVGW, focussed on pipelines)

## ▶ **Mission Statement**

### ▶ **Expert group on CO<sub>2</sub> specifications as spin off of the CCUS Forum process**

- ▶ Not aiming at the development of a standard (DIN, ISO, CEN, ...)
- ▶ Pointing out issues that have to be considered by a standard and making suggestions for how to formulate standards
- ▶ Difficult balance: Send the message “we can and must go ahead now” while pointing out areas of missing knowledge at the same time
- ▶ DG Energy will hopefully consider advice in future calls, one starting point of the upcoming discussion on a CCS Center of Excellence
- ▶ Report was completed end of June, was published online September 22<sup>nd</sup>
- ▶ <https://circabc.europa.eu/ui/group/75b4ad48-262d-455d-997a-7d5b1f4cf69c/library/13c2a475-c705-432d-8ca3-17ce799ba502/details>

## ► The Members

Name	Organisation
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Anaïs Faucher	Eurogas
<b>Andy Brown</b>	<b>Progressive Energy</b>
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Eric De Coninck	ArcelorMittal
Filip Neele	TNO
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Frank Wettland	Altera Infrastructure
<b>Harald Tatlik</b>	<b>Wintershall Dea</b>
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Stefan Federhen	HeidelbergMaterials
Steven Van Caekenberghe	Fluxys
Volker Hoenig	VDZ
Xavier Sturbois	Fluxys

Organization of the expert group: Per-Olof Granstrom / Charles-Albert Bareth

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## ▶ Guiding Principles

### ▶ Three (*plus one*) guiding principles

- ▶ Two-phase flow should be avoided as much as is practicable
- ▶ The formation of corrosive phases must be avoided
- ▶ The concentration of all impurities in a CO<sub>2</sub> stream should be specified to be such that their health and safety impact is always less than that of the carbon dioxide itself
- ▶ *Given limits, e.g., on impurities should be science based and traceable with at least a rough idea regarding their uncertainty*



## ▶ **Negotiable and Non-Negotiable Impurities**

### ▶ **Non-Negotiable Impurities**

- ▶ Formation of solids has to be avoided
- ▶ Corrosion has to be avoided
- ▶ Water and impurities that reduce the dew point need to be strictly limited
- ▶ Poisonous impurities have to be limited to levels that do not increase the toxicity of CO<sub>2</sub>

### ▶ **Negotiable Impurities**

- ▶ Non-condensable gases increase the pressure on the saturated liquid line
- ▶ High concentrations increase the cost of transport, but reduce the cost of CO<sub>2</sub> processing
- ▶ Optimisation has to consider whole chain cost
- ▶ Hub concepts versus processing to high purity before first transport

## ► Specifying the Level of Non-Condensable Gases

### ► Specifying the level of non-condensable gases

- Different non-condensable gases have a different impact on the pressure on the saturated liquid line
- The pressure on the saturated liquid line is particularly important for tank transport (medium pressure ship transport / rail cars)
- Define the minimum temperature required for liquefaction at a certain pressure rather than composition

### ► Conversion of standards

- In pipelines compositions will be measured, not saturation pressures
- A standard for the conversion needs to be defined from beginning on

## ▶ R&I Initiatives Transport

### ▶ Examples for identified research areas

- ▶ Flow and composition measurements in two phase systems
- ▶ Fast (sub second?) online composition measurement
- ▶ Hazardous impurities: Assessment of the health threat for combined exposure
- ▶ Effect of acid forming impurities on phase equilibria (at ppm level)
- ▶ Chemical reactions in mixed CO<sub>2</sub> streams, catalytic effects
- ▶ Formation of LLE / SLE at low temperature (glycols, in particular TEG, amines, ...)
- ▶ CO / CO<sub>2</sub> stress corrosion cracking?
- ▶ Corrosion without a corrosive phase?
- ▶ System analysis combining CO<sub>2</sub> transport (with impact of impurities), H<sub>2</sub> transport, regional availability of renewable energy

## ▶ Development of Standards

### ▶ Need for European standards

- ▶ So far, specifications for (impurities in) CO<sub>2</sub> are project specific
  - ▶ In some countries development of national standards (in Germany DVGW, focussed on pipelines)
  - ▶ National standardisation bodies and ISO are usually well connected
  - ▶ ISO is working on standards both for ship pipeline and for ship / tank transport
  - ▶ ISO standards will always be rather general, not detailed enough as basis for development
  - ▶ CEN process will cost much time, investment decisions have to be made soon
  - ▶ **DVGW tries to align national initiatives to come to a common understanding**
  - ▶ **Develop CEN standard on this common basis later on**
- ▶ Currently largely independent development of standards for pipeline and ship / tank transport in different communities – synergies for an optimal system might get lost

## ► **Treatment of Impurities in Standards**

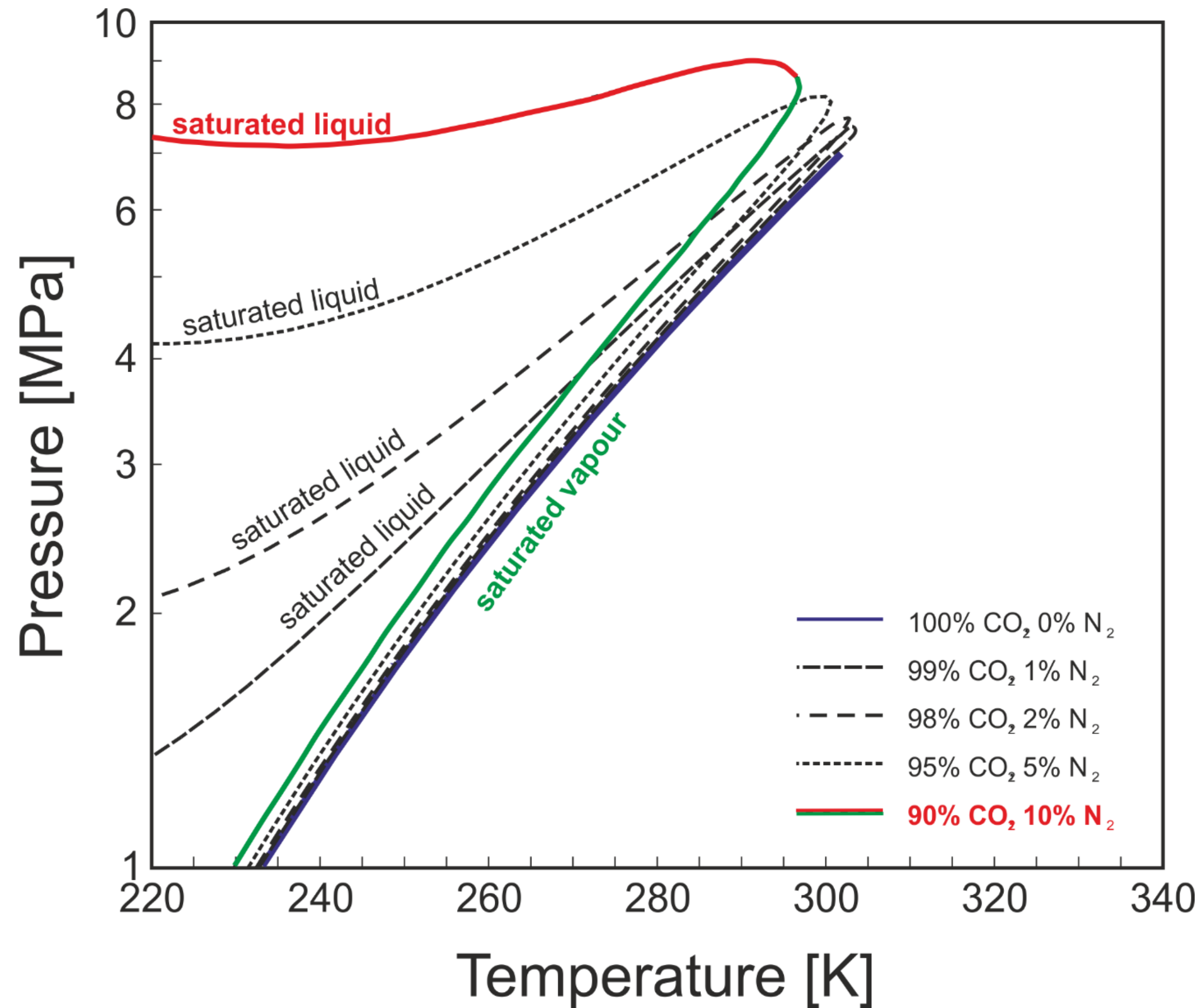
### ► **ISO standard (for pipeline transport) will likely ...**

- Contain a value for the minimum purity of CO<sub>2</sub>
- Not contain a list with strict limits for certain impurities
- Contain an appendix with examples for practically feasible compositions
- Specification of composition limits on national / CEN level, deviating agreements possible

### ► **An open question is how to deal with impurities that are not specifically listed**

- Northern Lights claims that substances not listed must not be contained (strictly!)
- Not a feasible approach for a network – different processes will always result in a variety of trace components (ppb range), which may partly be below current analytical limits
- Development of analytics or simply analysis considering trace components not looked at before must not become a challenge for made investments

# Thermophysical Properties of CO<sub>2</sub>-rich Mixtures



- Air components have a strong impact on phase equilibria
- The position of the dew line (saturated vapor) changes noticeably
- The position of the bubble line (saturated liquid) changes drastically
- Consequences, e.g., for centrifugal pumps
- **Arrest pressure** to avoid running ductile fracture depends on the pressure on the saturated liquid line

# GERG-2008 – Using a Natural Gas Standard for CCS

- Helmholtz-model for mixtures of up to 21 components by Kunz and Wagner (2012)
- General approach introduced independently by Lemmon & Tillner-Roth in mid 90's
  - Pure fluid equations of state (EOS)
  - Mixing rules for reduced input parameters  $\delta_m$  and  $\tau_m$

$$\alpha(\delta, \tau, \bar{x}) = \sum_{i=1}^N x_i \left[ \alpha_{oi}^0(\rho, T) + \ln x_i \right] + \sum_{i=1}^N x_i \alpha_{oi}^r(\delta_m, \tau_m) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta_m, \tau_m)$$

Methane (CH<sub>4</sub>)

**Nitrogen (N<sub>2</sub>)**

**Carbon dioxide (CO<sub>2</sub>)**

Ethane (C<sub>2</sub>H<sub>6</sub>)

Propane (C<sub>3</sub>H<sub>8</sub>)

n-Butane (n-C<sub>4</sub>H<sub>10</sub>)

Isobutane (i-C<sub>4</sub>H<sub>10</sub>)

n-Pentane (n-C<sub>5</sub>H<sub>12</sub>)

Isopentane (i-C<sub>5</sub>H<sub>12</sub>)

n-Hexane (n-C<sub>6</sub>H<sub>14</sub>)

n-Heptane (n-C<sub>7</sub>H<sub>16</sub>)

n-Octane (n-C<sub>8</sub>H<sub>18</sub>)

n-Nonane (n-C<sub>9</sub>H<sub>20</sub>)

n-Decane (n-C<sub>10</sub>H<sub>22</sub>)

**Hydrogen (H<sub>2</sub>)**

**Carbon monoxide (CO)**

Hydrogen sulphide (H<sub>2</sub>S)

**Water (H<sub>2</sub>O)**

**Oxygen (O<sub>2</sub>)**

**Argon (Ar)**

Helium (He)

# GERG-2008 – Using a Natural Gas Standard for CCS

- Helmholtz-model for mixtures of up to 21 components by Kunz and Wagner (2012)
- General approach introduced independently by Lemmon & Tillner-Roth in mid 90's
  - Pure fluid equations of state (EOS)
  - Mixing rules for reduced input parameters  $\delta_m$  and  $\tau_m$

four parameter extended corresponding states

departure function

$$\alpha(\delta, \tau, \bar{x}) = \sum_{i=1}^N x_i \left[ \alpha_{oi}^0(\rho, T) + \ln x_i \right] + \sum_{i=1}^N x_i \alpha_{oi}^r(\delta_m, \tau_m) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N x_i x_j F_{ij} \alpha_{ij}^r(\delta_m, \tau_m)$$

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**Hydrogen (H<sub>2</sub>)**

**Carbon monoxide (CO)**

Hydrogen sulphide (H<sub>2</sub>S)

**Water (H<sub>2</sub>O)**

**Oxygen (O<sub>2</sub>)**

Argon (Ar)

(He)

**Standard for natural-gas properties according to ISO 20765-2:2015**

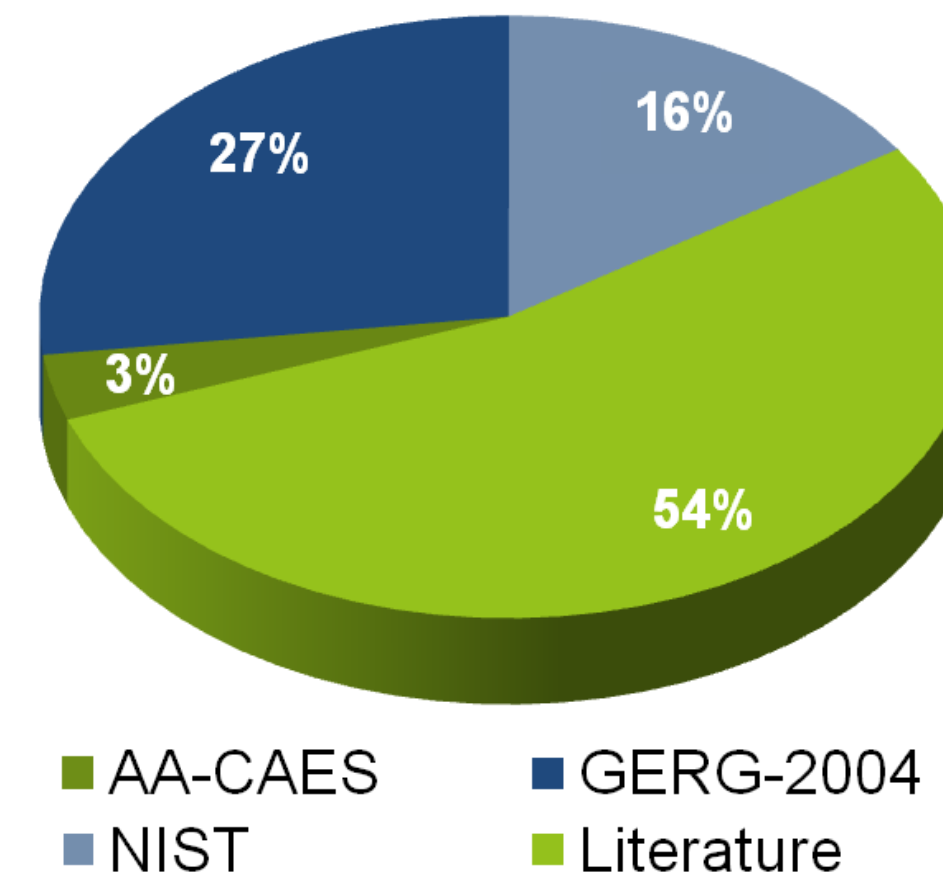
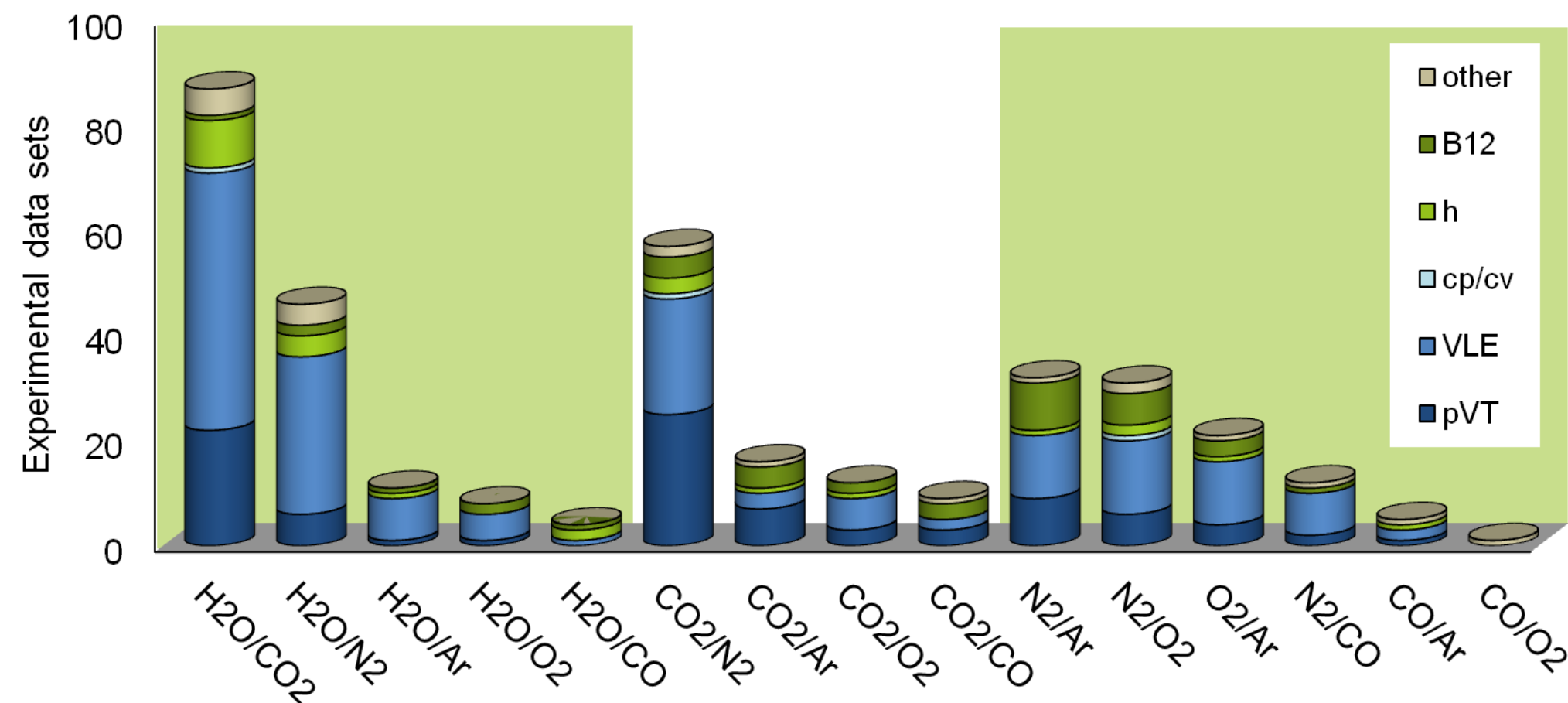


# EOS-CG – A Model for CO<sub>2</sub>-Rich Mixtures

EOS-CG describes 15 binary Systems, is compatible to GERG-2008 for other systems

	H <sub>2</sub> O	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	Ar
CO	▲	●	●	■	■
Ar	●	★	●	●	
O <sub>2</sub>	▲	●			
N <sub>2</sub>	★				
CO <sub>2</sub>	★				

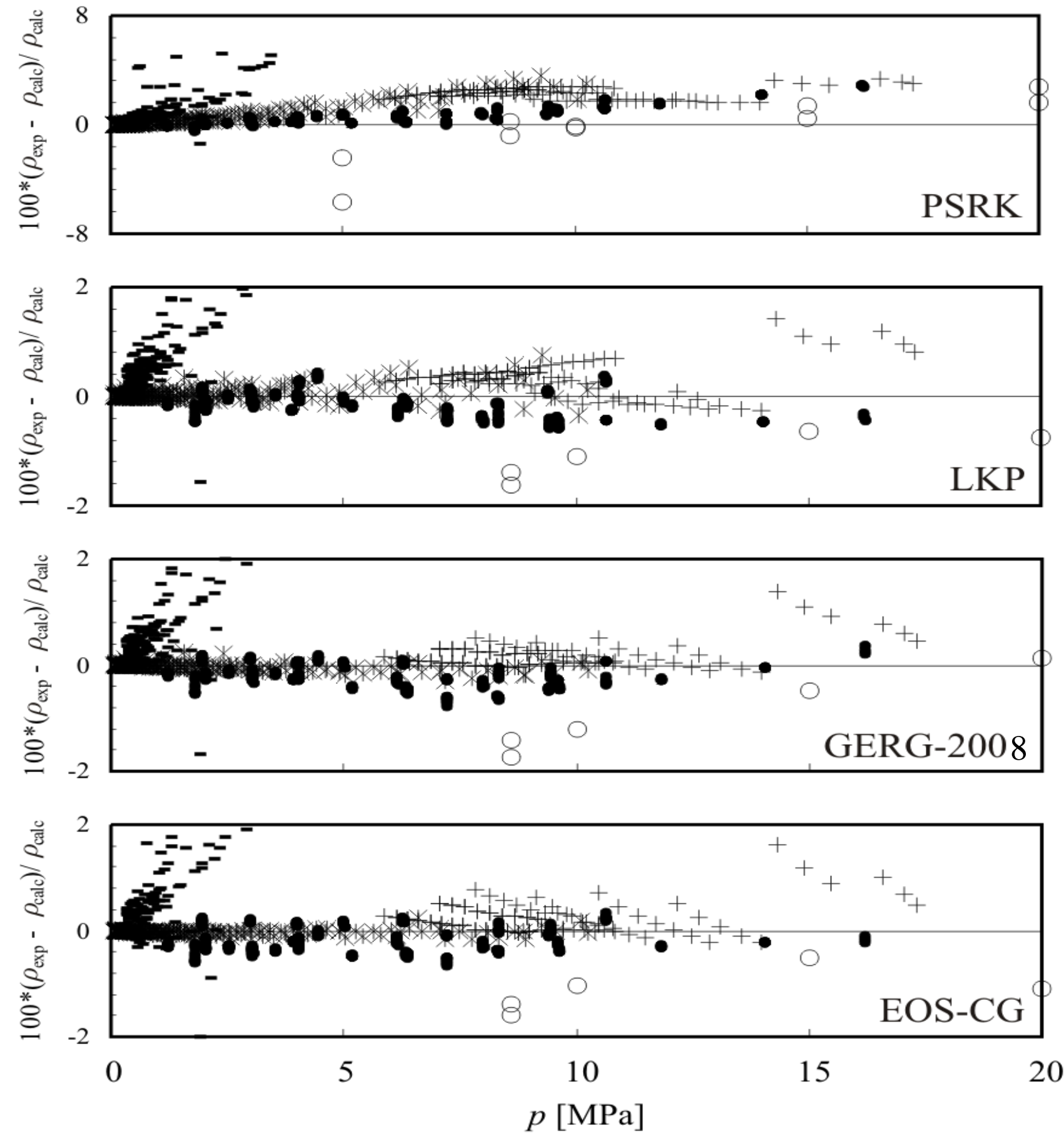
- ★ Binary specific departure function  $\alpha_{ij}^r$
- ▲ Common departure function with fitted  $F_{ij}$
- Fitted reducing functions  $\rho_r$  and  $T_r$
- General combination rules for  $\rho_r$  and  $T_r$



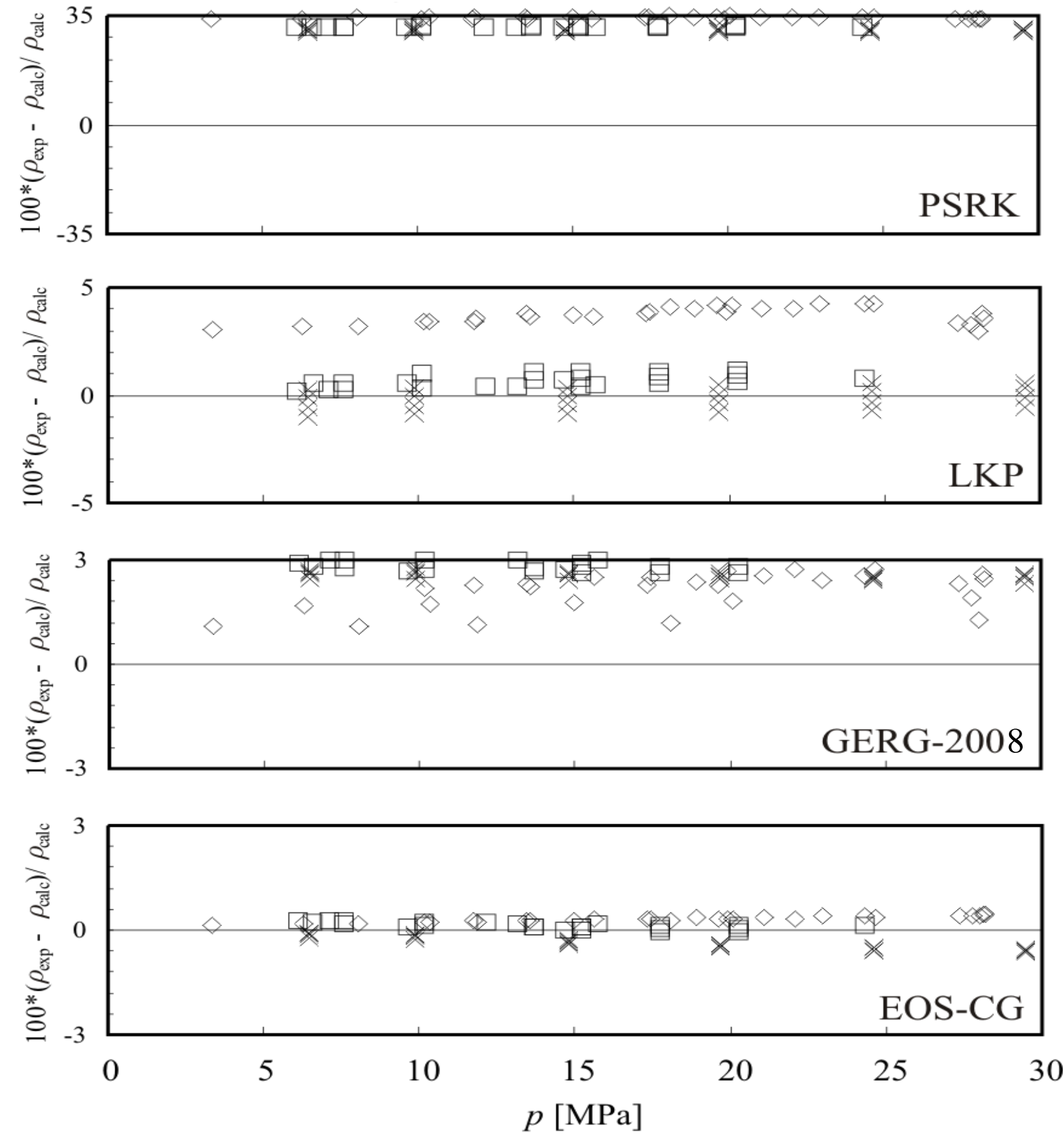
Gernert (2013), Gernert & Span (2015)

# EOS-CG – A Model for CO<sub>2</sub>-Rich Mixtures

Gas Densities ( $T < 600$  K)



Liquid Densities ( $278$  K  $< T < 332$  K)



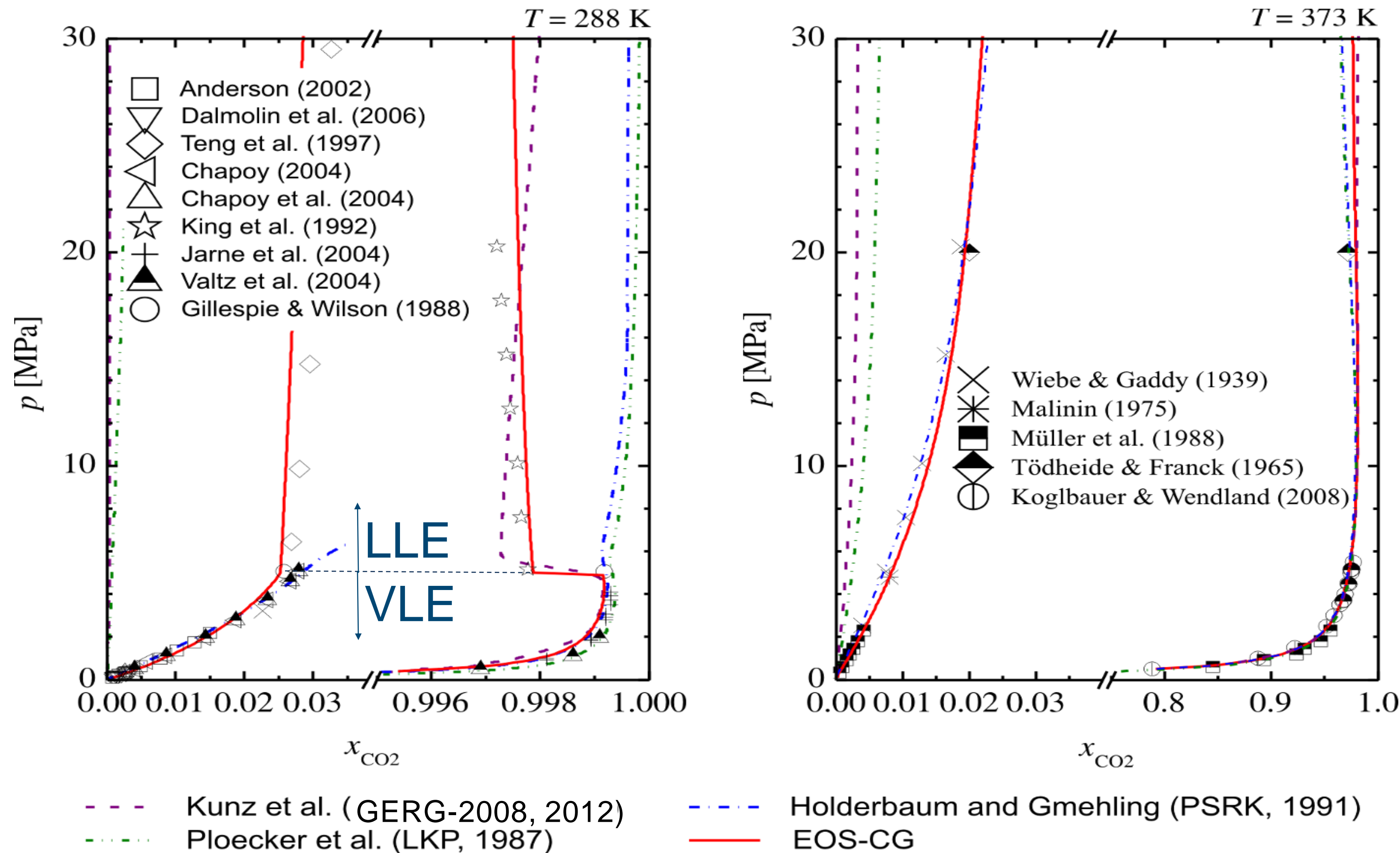
\* Patel & Eubank (1988)      - Zawisza & Malesinska (1981)  
 + Fenghour et al. (1994)      o Zhakirov (1984)  
 • McLinden (2011)

◇ Li et al. (2004)    □ King et al. (1992)    × Teng et al. (1997)

- Most significant improvements for the System CO<sub>2</sub> / H<sub>2</sub>O
- Gas densities are described well by different EOS
- Only EOS-CG describes liquid densities equally good

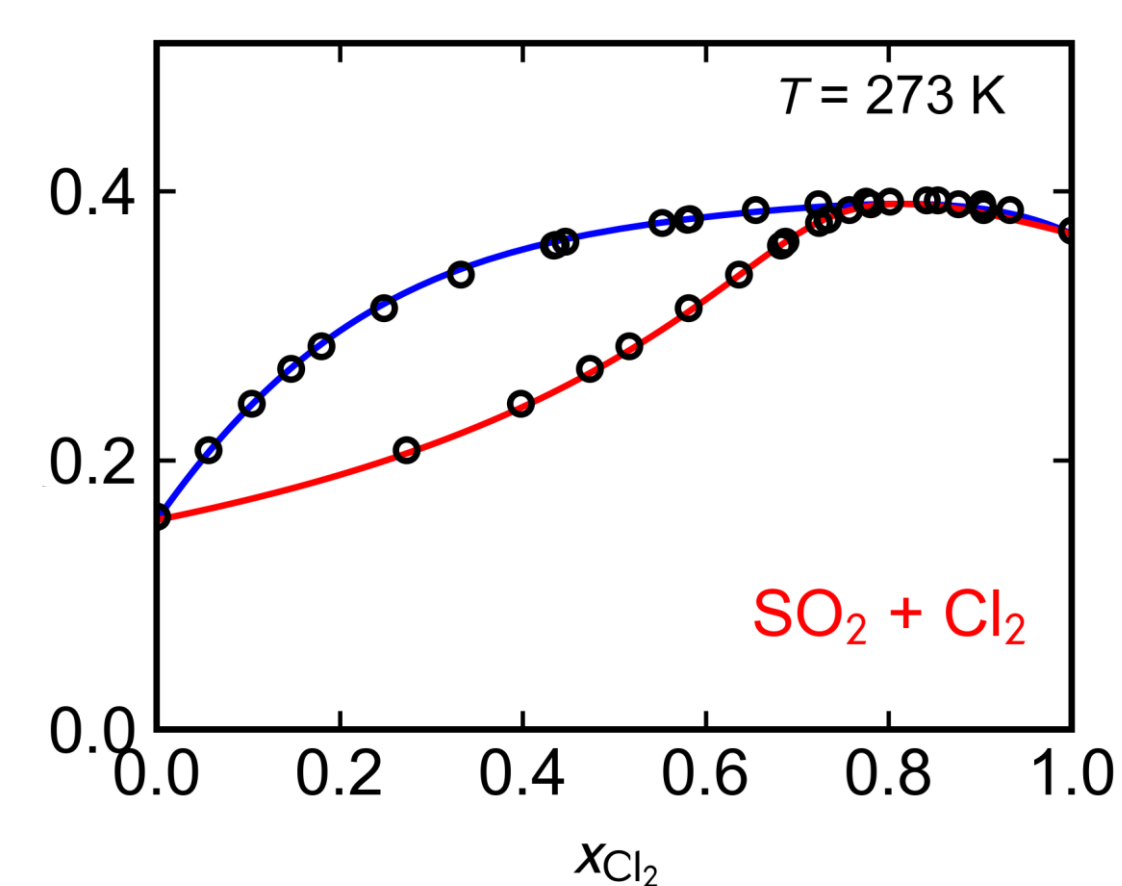
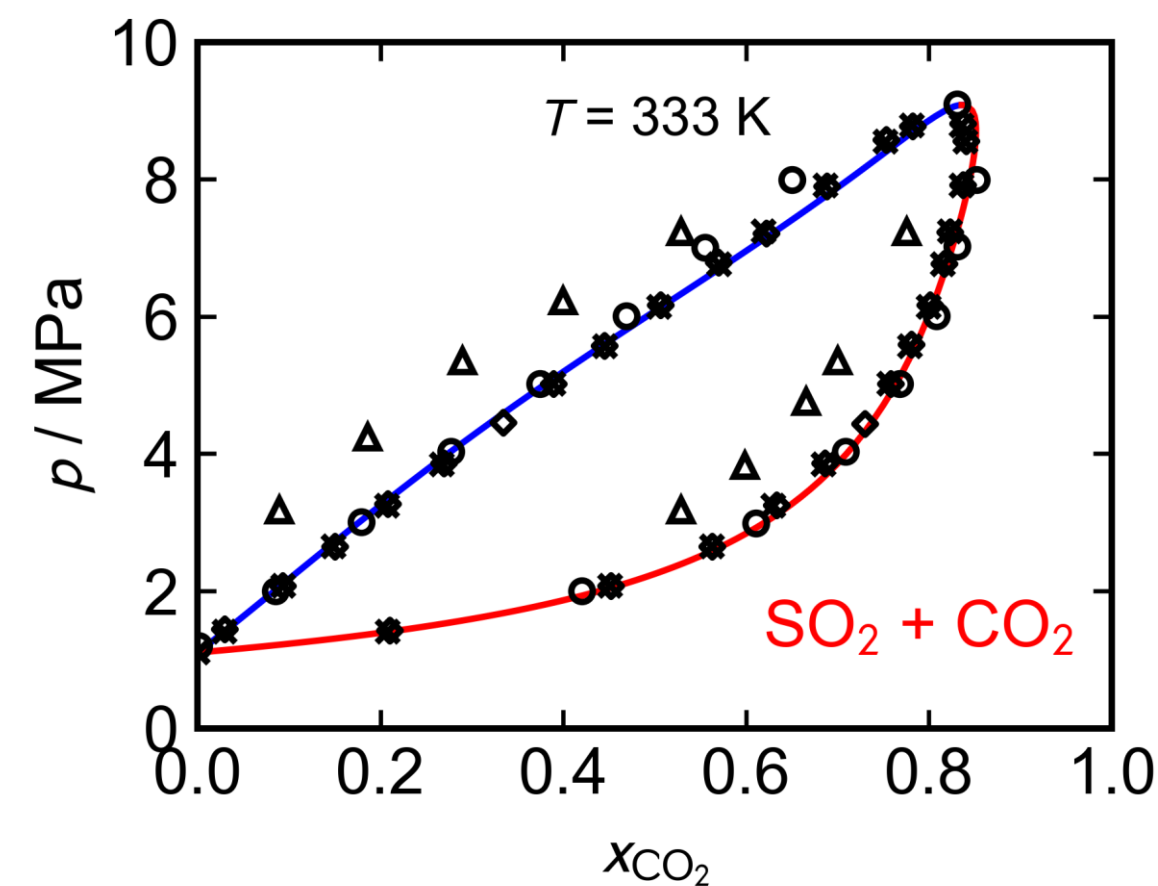
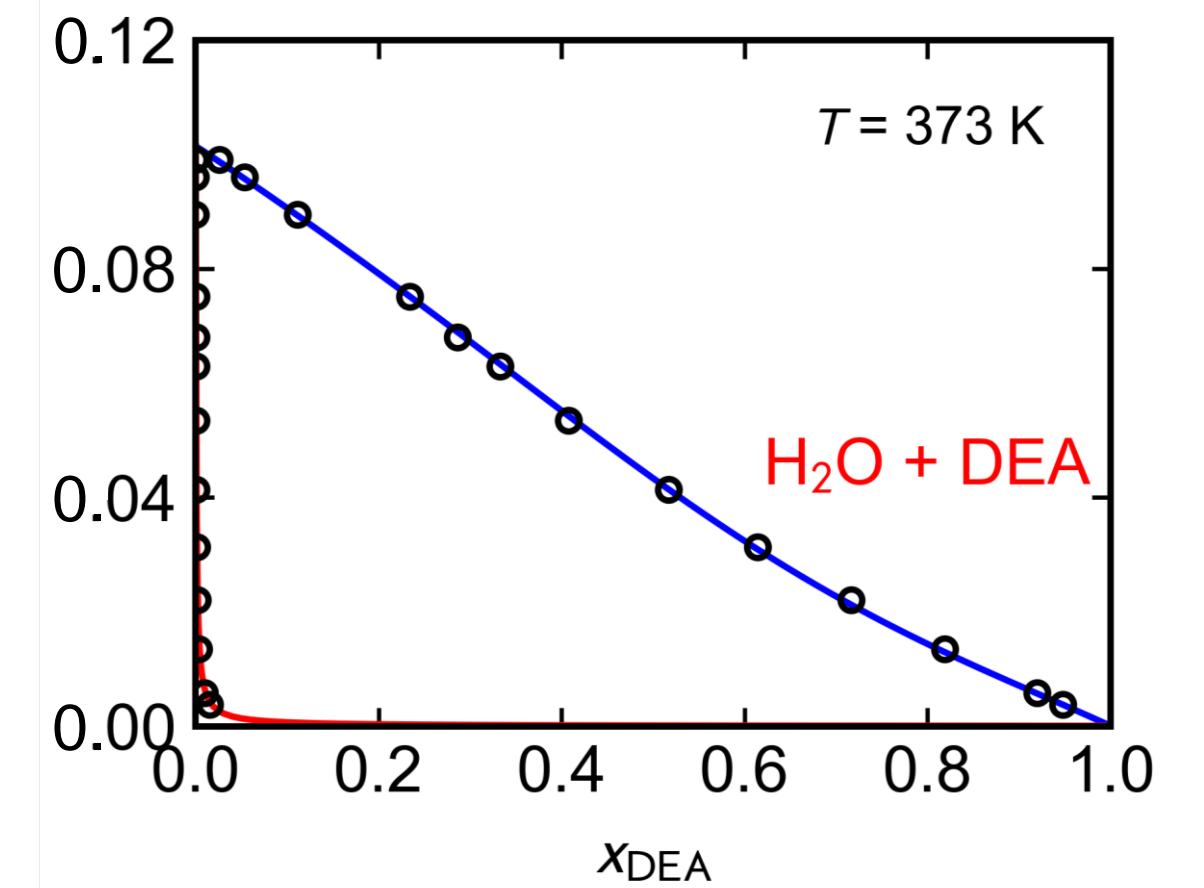
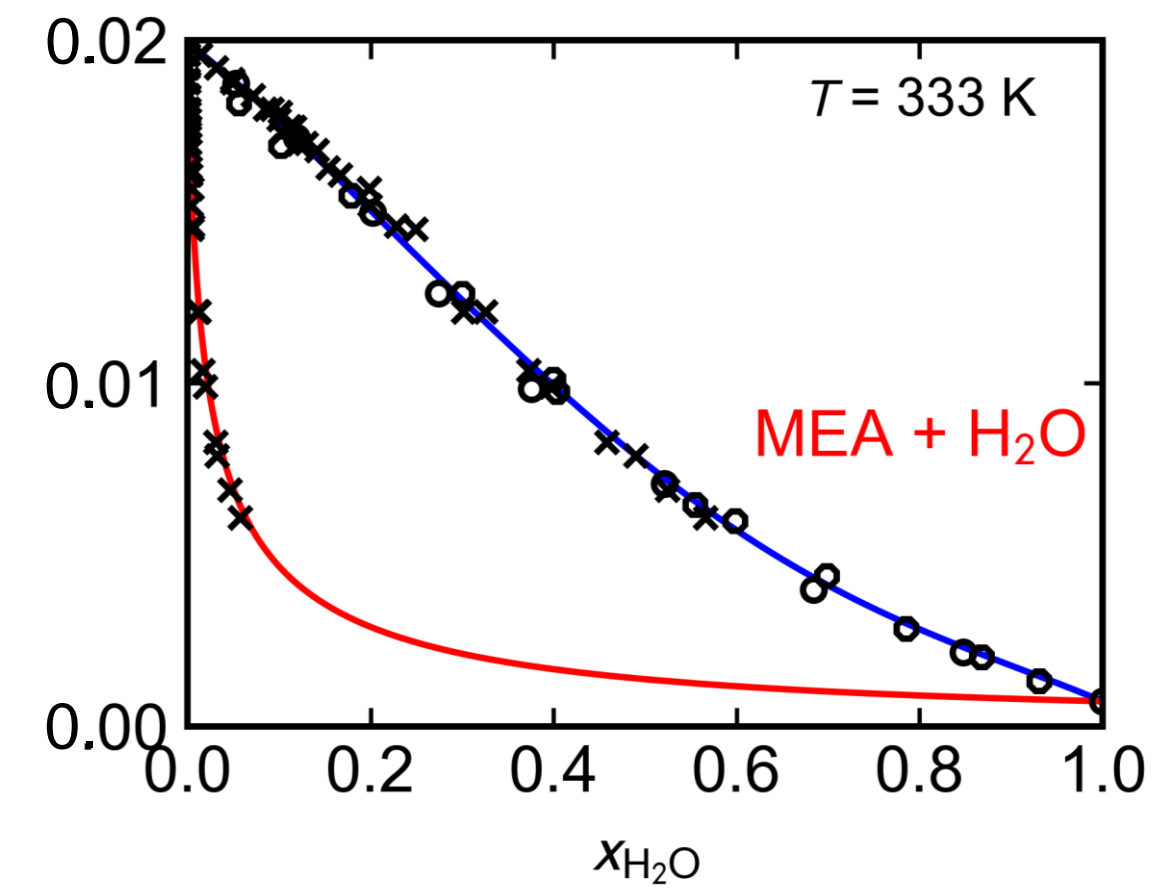
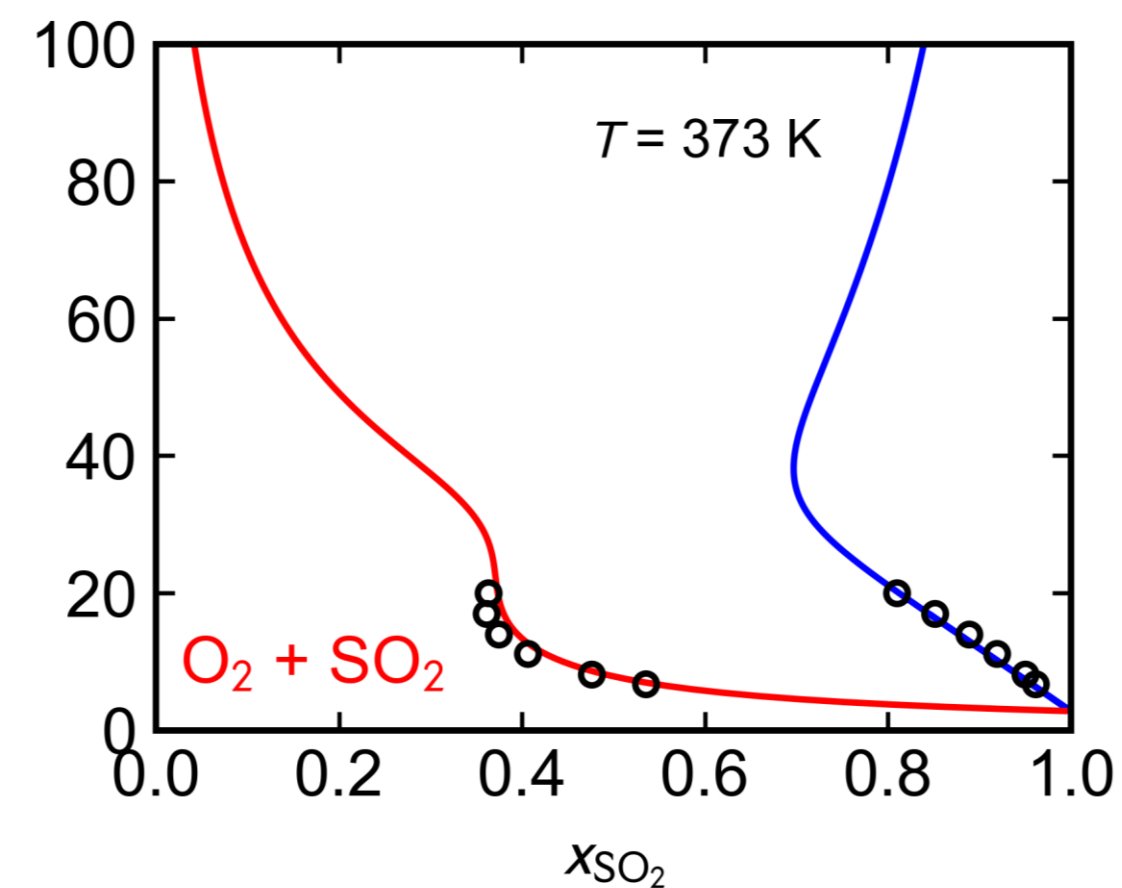
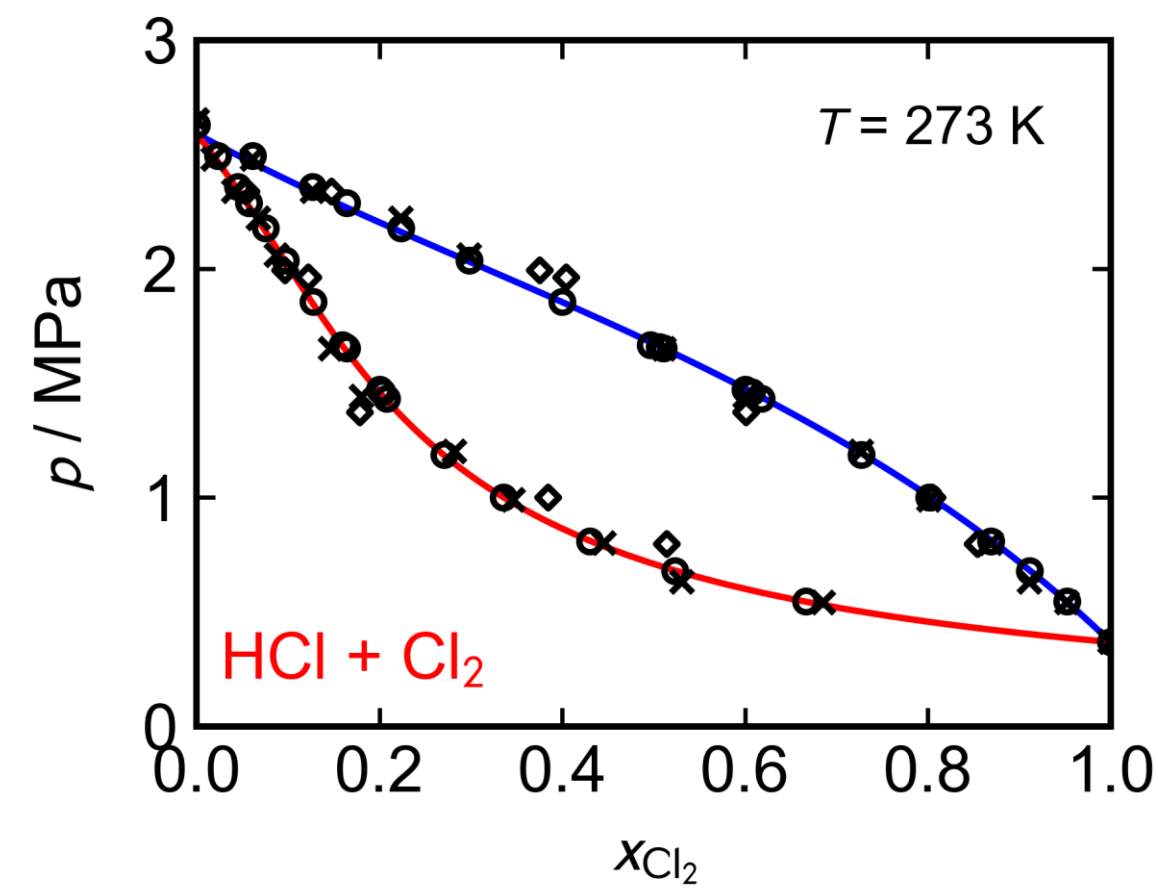
Gernert (2013), Gernert & Span (2015)

# EOS-CG – A Model for CO<sub>2</sub>-Rich Mixtures



- Most significant improvements for the System CO<sub>2</sub> / H<sub>2</sub>O
  - VLE / LLE equilibria need to be calculated
  - CO<sub>2</sub>-rich phase described well by different models
  - H<sub>2</sub>O-rich phase described well by EOS-CG
- Gernert (2013), Gernert & Span (2015)

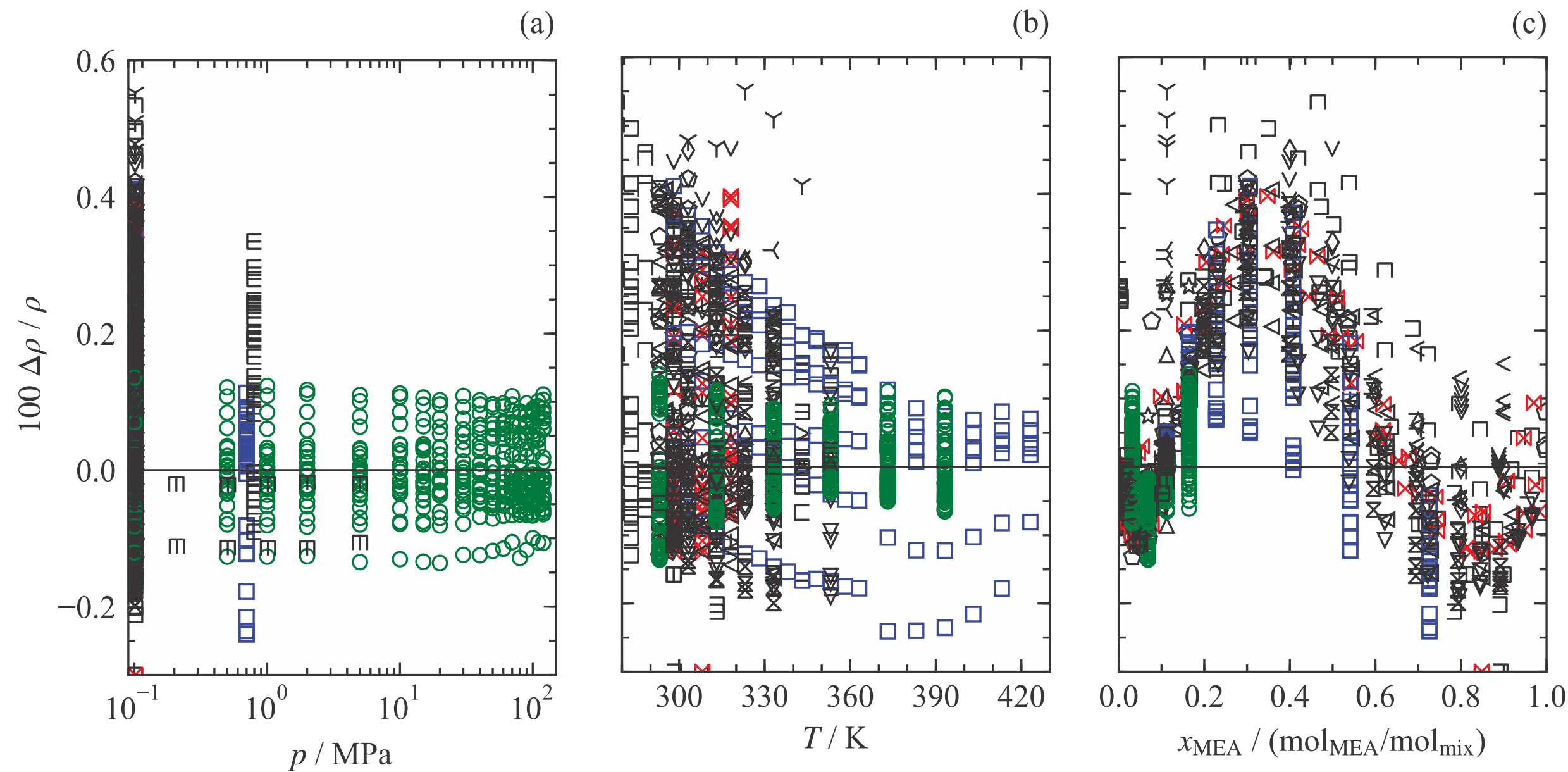
# Consideration of Minor Impurities



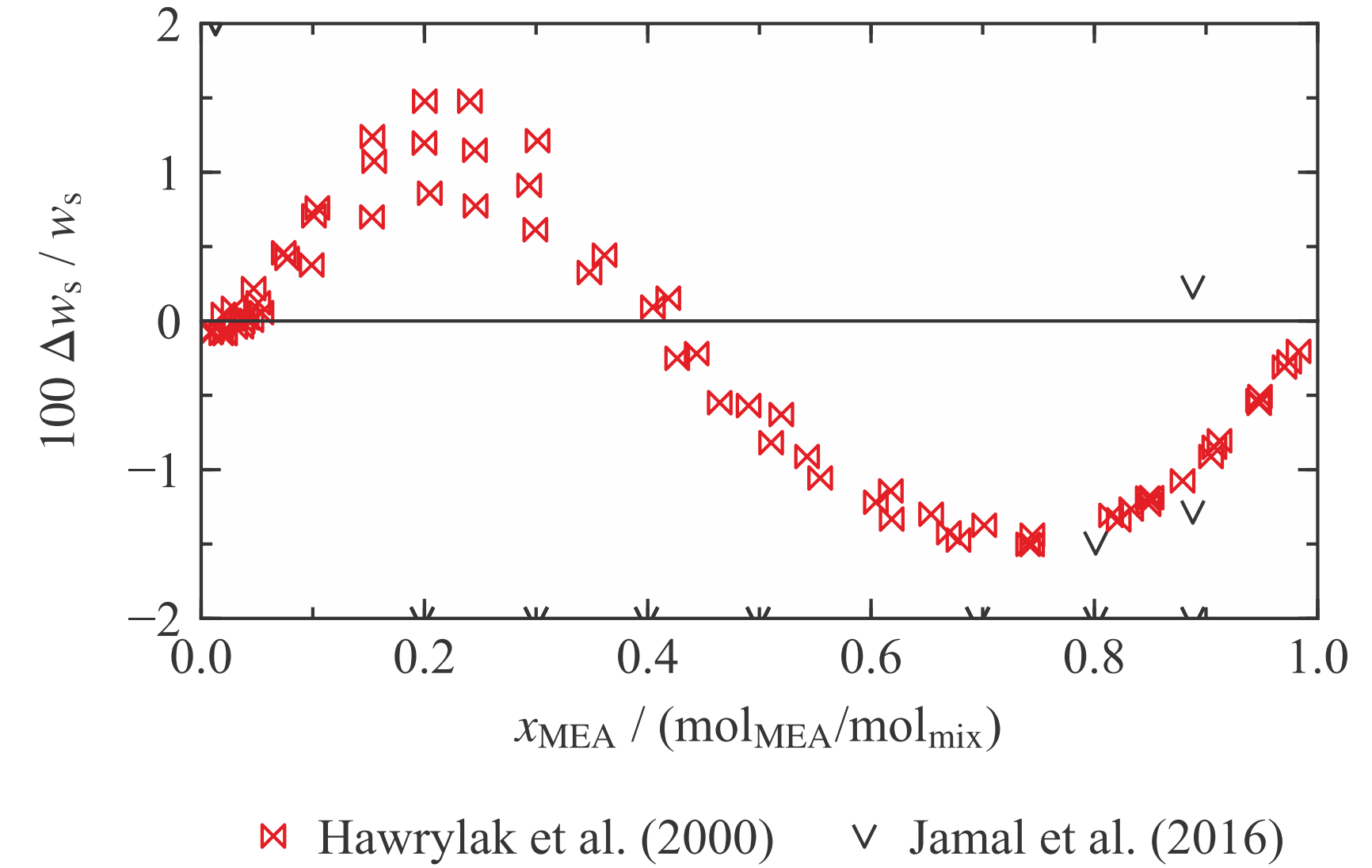
- Minor impurities mostly relevant for VLE
- Available data limit the accuracy
- Multiparameter models can describe the systems, but advantages shrink

Herrig et al. (2018)

# Consideration of Minor Impurities



⊖ Amundsen et al. (2009)	⊗ Ju et al. (2018)	△ Mandal et al. (2003)	◇ Tseng and Thompson (1964)
⊓ Arcis et al. (2011)	⊓ Kapadi et al. (2002)	⋖ Muraleedharan et al. (2012)	⊓ Wadi and Kathuria (1992)
□ Han et al. (2012)	◇ Lee and Lin (1995)	⊓ Page et al. (1993)	☆ Weiland et al. (1998)
⊓ Hartono et al. (2014)	⊓ Li and Lie (1994)	⋖ Pouryousefi and Idem (2008)	⊗ Yin et al. (2017)
⊗ Hawrylak et al. (2000)	⋖ Ma et al. (2019)	○ Sobrino et al. (2016)	^ Zhang et al. (2015)
∨ Jamal et al. (2016)	∇ Maham et al. (1994)	▷ Song et al. (1996)	⋈ Zhao et al. (2010)
⊓ Jayarathna et al. (2013)	⊓ Maham et al. (2002)	⊓ Touhara et al. (1982)	



- Where data are available in homogeneous regions, they are represented quite well
- Example: MEA / Water, density and speed of sound

Neumann et al. (2023)

# Consideration of Minor Impurities

		methyl diethanolamine	ammonia	chlorine	hydrogen chloride	diethanolamine	monoethanolamine	sulfur dioxide	hydrogen sulfide	methane	hydrogen	carbon monoxide	argon	oxygen	nitrogen	water
major components	carbon dioxide	•	•	H	H	H	N2	H	KW	KW	B	S	L	GS	KW	GS
	water	•	R	H	H	•	•	H	H	H	KW	GS	GS	GS	GS	
	nitrogen	•	N1	H	H	H	H	H	KW	KW	B	GS	GS	KW		
	oxygen	•	N1	H	H	H	H	H	KW	KW	KW	GS	GS			
	argon	•	N1	H	H	H	H	H	KW	KW	KW	KW				
↕	carbon monoxide	•	N1	H	H	H	H	H	KW	KW	B					
	hydrogen	•	N1	H	H	H	H	H	KW	B						
	methane	•	N1	H	H	H	H	H	KW							
minor components	hydrogen sulfide	•	N1	H	H	H	H	H								
	sulfur dioxide	•	N1	H	H	H	H									
	monoethanolamine	•	N1	H	H	H										
	diethanolamine	•	N1	H	H											
	hydrogen chloride	•	N1	H												
	chlorine	•	N1													
	ammonia	•														

Yellow	Specific departure function
Orange	Generalized departure function
Blue	Adjusted reducing functions
Grey	Lorentz-Berthelot combining rules
Green	Linear combining rules

- The matrix of described systems has been extended
- In many cases hardly any data available
- (Weakly) reacting systems can be described on an empirical basis

•	This work
H	Herrig
KW	Kunz and Wagner
GS	Gernert and Span
N1	Neumann et al.

B	Beckmüller et al.
N2	Neumann et al.
R	Published within Refprop
S	Souza et al.
L	Løvseth et al.

Neumann et al. (2023)

# Questions?

## ▶ CO<sub>2</sub> Specifications for Transport and Thermodynamic Properties

26.10.2023

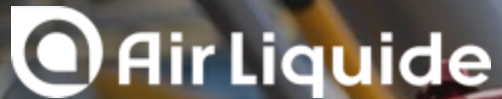
Online

Roland Span

Sub-Project Leader CO<sub>2</sub> Transport  
EERA JP CCS

Chair of Thermodynamics  
Ruhr-University Bochum





# CCUS Process & Metrological challenges from Industry Perspective

METCCUS Seminar 26.10.2023

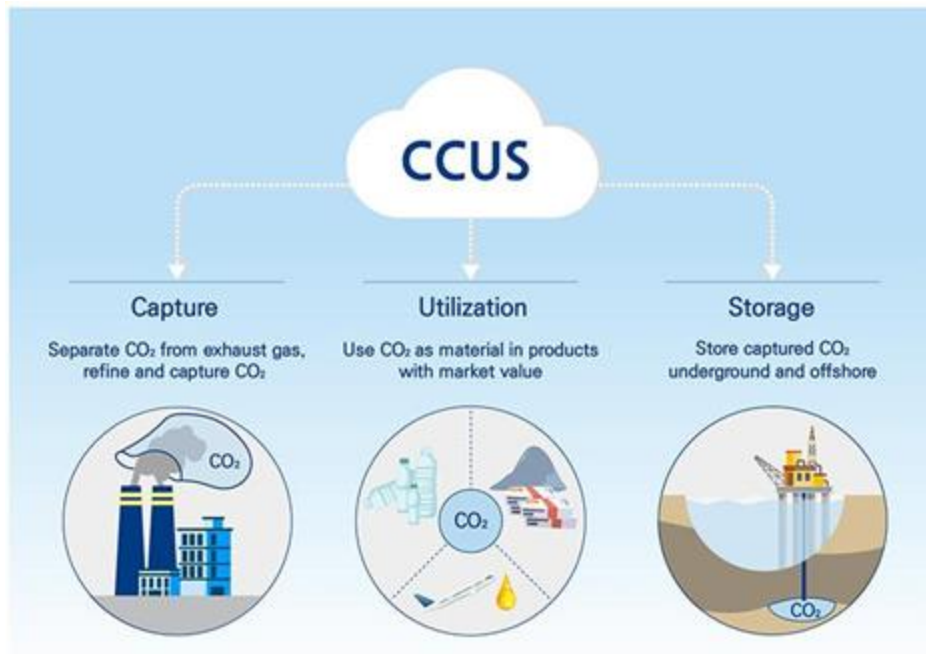
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*Martine Carré - Scientific Director Analytical Science  
Lucie Chaubet - Pole Manager Low Carbon Hydrogen*



# Contents

- ❑ Air Liquide R&D in brief
- ❑ CCUS solutions portfolio
- ❑ Impurity Management
- ❑ Metrological challenges





---

# Air Liquide R&D

# Air Liquide: A world leader in gases, technologies, and services for...



## INDUSTRY

**Sustainable solutions for a wide range of industrial processes of our customers** (energy, metals, food, chemicals, automotive, pharmaceuticals, etc.) **and for transports**



## HEALTH

**Patients at home**  
**Hospitals**  
**Specialty ingredients**

©Adrien Daste

# R&D KEY FIGURES

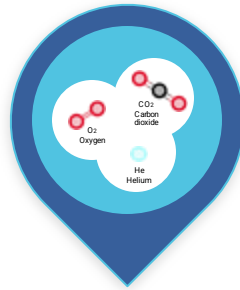
AS OF DECEMBER 2022



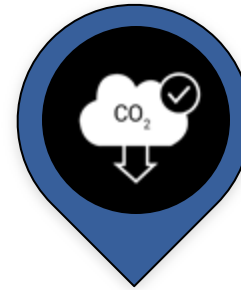
**5** CAMPUSES  
&  
**3** SATELLITES



**60%**  
R&D PROJECTS CONDUCTED IN  
PARTNERSHIPS  
with laboratories, start-ups,  
industrial players and customers



**18**  
ESSENTIAL  
SMALL  
MOLECULES



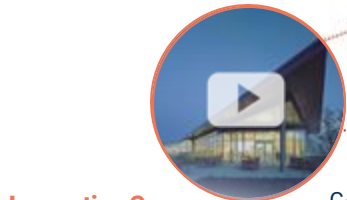
**60%**  
R&D PORTFOLIO IS  
DEVOTED TO REDUCE  
CO2 EMISSIONS\*



**557**  
EMPLOYEES

*\*by reducing the carbon content of Air Liquide products or those of its customers*

# INNOVATION CAMPUSES AROUND THE WORLD



**Innovation Campus Delaware** (2007)  
81 R&D People +  
3 R&D employees at  
the Montreal  
Satellite

Getting  
Closer to Airgas  
& its 1 M Customers  
1 satellite in  
Canada (Montréal)

**Innovation Campus Paris** (1970 / 2018\*)  
313 R&D People

Our flagship  
(50% of our resources)  
is at the heart of one of  
the biggest European  
innovation ecosystems.  
+ Host Accelair: a deep-tech  
startups Accelerator  
1 satellite in Germany  
(Krefeld)



**Innovation Campus Frankfurt** (1936 / 2008)  
59 R&D People

Energy  
processes  
within  
1st european  
economy



Leverage  
the Chinese  
Tech Powerhouse

**Innovation Campus Shanghai** (2005 / 2016\*)  
49 R&D People



**Innovation Campus Tokyo** (1986 / 2019\*)  
45 R&D People

Step change  
our presence  
in Japanese Tech  
Ecosystem  
1 satellite in Korea  
(Seoul) and 1 in Taiwan

\*Renovation date

# INNOVATION CAMPUS FRANKFURT

**EXPERTISE :** Science, Methods & Tools, Experiments, Large-scale industrial operations



## Science:

Process engineering, chemistry, analytics, catalysis, simulation, applied math & data science



## Methods & Tools:

LCA (Life Cycle Assessment), TEA (Techno Economic Analysis), digital tools, process simulation



## Experiments:

pilot plants, lab-scale, analytics, ...



Knowledge of **large-scale industrial operation**

CAMPUS STRATEGY based on 2 axes : **carbon management and low carbon emission + 3 essential small molecules**





# INNOVATION CAMPUS PARIS

59 Laboratories



8 technical platforms

Gas Security - Process Engineering - Computational and data sciences - Material qualification- Combustion - Food production - Additive production- - Gas Analysis



350

Persons

Découvrez le campus en [vidéo](#)



# CCUS Solutions portfolio



# CO2 value chain

## CO<sub>2</sub> SOURCES



### AIR LIQUIDE EMISSIONS



### CUSTOMERS' EMISSIONS

#### REFINING / CHEMICAL



#### CEMENT



#### POWER



#### MARITIME



#### BIOMASS



## CAPTURE, LIQUEFACTION AND TRANSPORT



### CAPTURE & PURIFICATION



#### ADSORPTION

#### ABSORPTION

#### MEMBRANES

#### CRYOGENIC

### LIQUEFACTION / COMPRESSION



### ROAD/TRAIN TRANSPORT



### MARITIME TRANSPORT



### PIPELINE



## UTILIZATION / SEQUESTRATION



### UTILIZATION (CCU)



#### CHEMICAL

CO / SYNGAS

METHANOL

EFUELS

PLASTICS

CO<sub>2</sub>

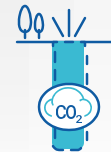
FOOD INGREDIENTS

AGRICULTURE

ENHANCED OIL RECOVERY

PHARMA

### SEQUESTRATION (CCS)



DEEP SALINE AQUIFERS

DEPLETED OIL OR GAS RESERVES

MINERALIZATION

# Air Liquide in the CCUS value chain

Capture

Pressurisation /  
Liquefaction

Transport / Distribution



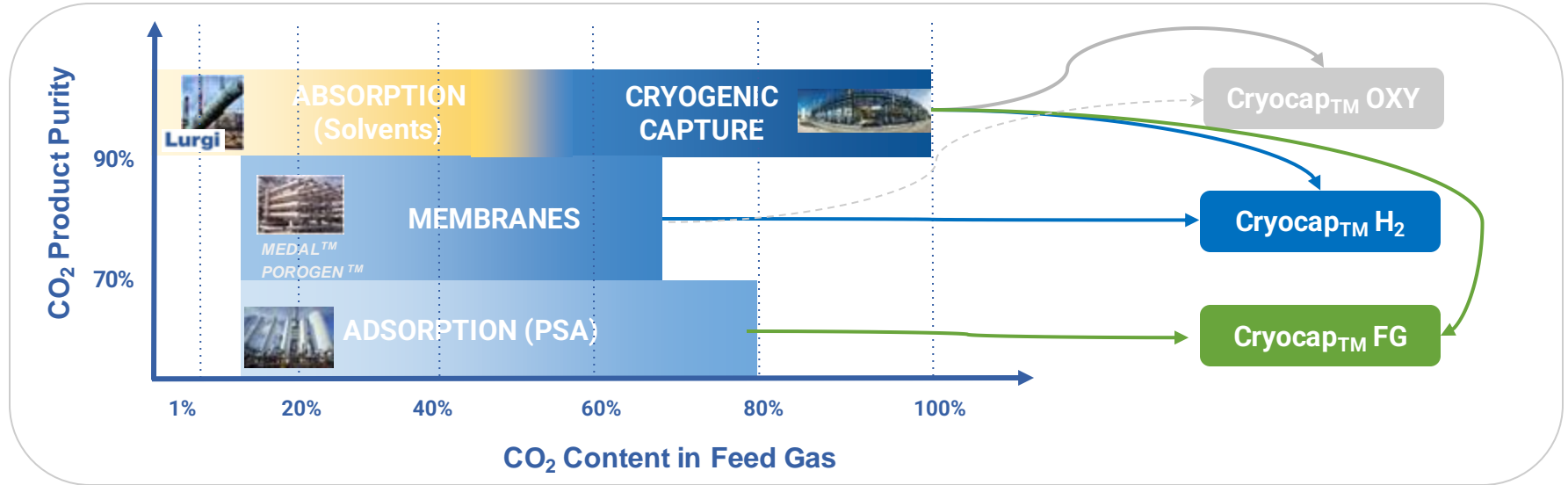
## Air Liquide expertise:

- Various CO2 capture technologies (Cryocap FG, H<sub>2</sub>, Oxy, Steel Amine wash, Rectisol) for different flue gas compositions
- CO2 compression, liquefaction and storage expertise
- CO2 pipeline experience

## Air Liquide motivation:

- Carbon Capture for own plants and as a service
- Reduction CO2 emissions -33% compared to 2020 by 2035

# Combining technologies for lowering CAPEX and OPEX



**Absorption:** The most suitable solution for low concentrated feed gas

**Cryocap™** combines cryogenic with membranes & adsorption, addressing any CO<sub>2</sub>% > 15%, electrical power only.

Can produce HP CO<sub>2</sub> or Liq CO<sub>2</sub> at marginal extra cost.

**HP CO<sub>2</sub>/Liq CO<sub>2</sub>: Looking for synergies between capture and compression / liquefaction steps is key**

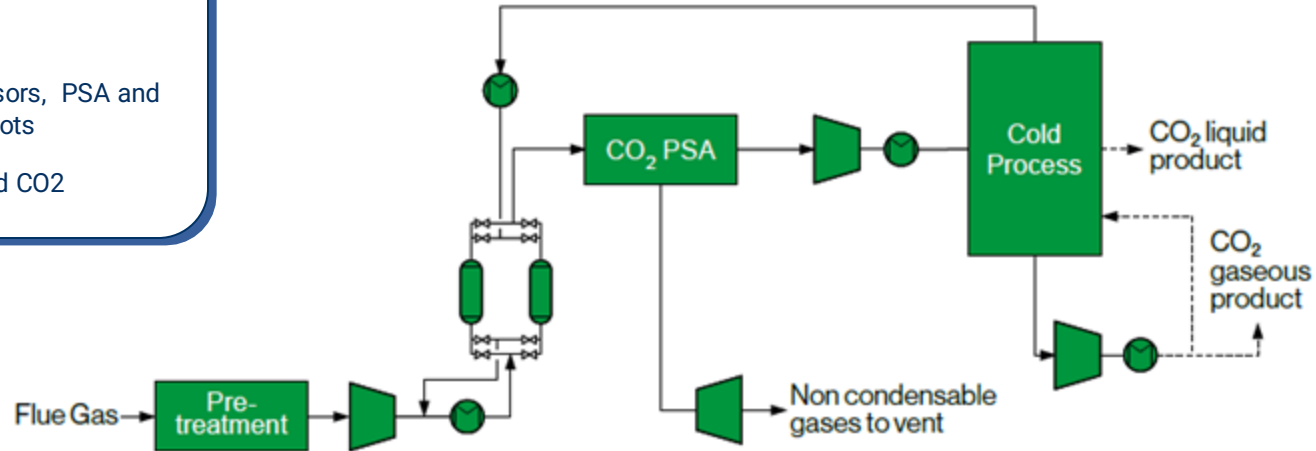
# Cryocap™ FG: CO2 capture from flue gas (15%-40% CO2)

## □ Technical highlights:

- Suitable for any flue gas with > 15mol% CO2 (dry basis): SMR, cement, limestone
- Electrically driven solution
- Gaseous or liquid CO2
- CO2 capture rate: 90% to 95%
- Compact & Flexible footprint: Compressors, PSA and Coldbox can be located in 3 different plots
- Range: min 400 tpd CO2 - max 5000 tpd CO2

## □ Indicative utility figures

- Gas CO2 at ~30 bara: 310 kWh/tCO2
- Liq. CO2: 390 to 450 kWh/tCO2



# Selected recent references - Carbon Capture on cement / lime applications

## Ste Genevieve

- CO2 capture from a single line kiln
- Cryocap FG: 10,000 tpd CO2
- Capture rate: 95%



## Lime kiln

- CO2 capture from a lime kiln
- Cryocap FG: 1,650 tpd CO2
- Capture rate: 95%

## EQIOM

- CO2 capture from cement plant converted to oxycombustion
- Cryocap Oxy: 3,000 tpd CO2
- Capture rate: 95%



# Air Liquide's involvement in CCS projects & sink developments

## Northern Lights



### Starvenger

**Project:** Northern Lights consortium project focuses on transport, reception and permanent storage of CO<sub>2</sub> in a reservoir in the northern part of the North Sea.

**Role AL:** evaluating CO<sub>2</sub> capture and transport



## Porthos



### Rotterdam

**Project:** Open access CO<sub>2</sub> transport and storage system through a public-private initiative by PoR.

**Role AL:** evaluating CO<sub>2</sub> capture, aggregation and transport



## Antwerp@C



### Antwerp

**Project:** Consortium of industrial players to develop- feasibility study of building CO<sub>2</sub> infrastructure for CCS(U)

**Role AL:** evaluating CO<sub>2</sub> capture, aggregation and transport





# Impurities management

# Typical impurities in flue gas and process off-gases

	<b>Refinery FCC flue gas</b>	<b>Steel Blast Furnace gas</b>	<b>Steel Coke Oven gas</b>	<b>Cement Kiln Off-gas</b>
<b>Main components</b>	N <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O	N <sub>2</sub> , CO <sub>2</sub> , CO, H <sub>2</sub> , H <sub>2</sub> O	H <sub>2</sub> , N <sub>2</sub> , CO, CH <sub>4</sub> , CO <sub>2</sub>	N <sub>2</sub> , CO <sub>2</sub> , O <sub>2</sub> , H <sub>2</sub> O
<b>Typical impurities</b>	<ul style="list-style-type: none"> <li>- SO<sub>x</sub></li> <li>- NO<sub>x</sub>, HCN</li> <li>- unburnt CO</li> <li>- O<sub>2</sub></li> <li>- Dust</li> </ul>	<ul style="list-style-type: none"> <li>- H<sub>2</sub>S, COS, SO<sub>x</sub></li> <li>- NO<sub>x</sub>, NH<sub>3</sub>, HCN</li> <li>- O<sub>2</sub></li> <li>- Hydrocarbons including BTEX</li> <li>- Halides</li> <li>- Metals, metal carbonyls</li> <li>- Dust</li> </ul>	<ul style="list-style-type: none"> <li>- H<sub>2</sub>S, COS, C<sub>2</sub>S, mercaptans</li> <li>- NO<sub>x</sub>, HCN, NH<sub>3</sub></li> <li>- O<sub>2</sub></li> <li>- Hydrocarbons including BTEX</li> <li>- H<sub>2</sub>O</li> </ul>	<ul style="list-style-type: none"> <li>- SO<sub>2</sub></li> <li>- NO<sub>x</sub></li> <li>- CO</li> <li>- HCl</li> <li>- Metals</li> <li>- Dust</li> </ul>



# Key questions of impurity management

Compositions, variability vs feedstock, operation constraints

Fate of impurities in CO<sub>2</sub> separation process

Gas polishing processes

Specifications



Steel



CO<sub>2</sub>

CO<sub>2</sub> SOURCE

REMOVAL OF IMPURITIES

CARBON CAPTURE

REMOVAL OF IMPURITIES

TRANSPORT

STORAGE UTILIZATION

Conversion to chemicals



Chemicals industries



Power/ Cement



H<sub>2</sub> Production

- Choice of the materials
- Risks of freezing
- Risks of plugging
- Recycles: prevent accumulation
- CO<sub>2</sub> removal: concentration phenomena



Greenhouses



Food & Beverage

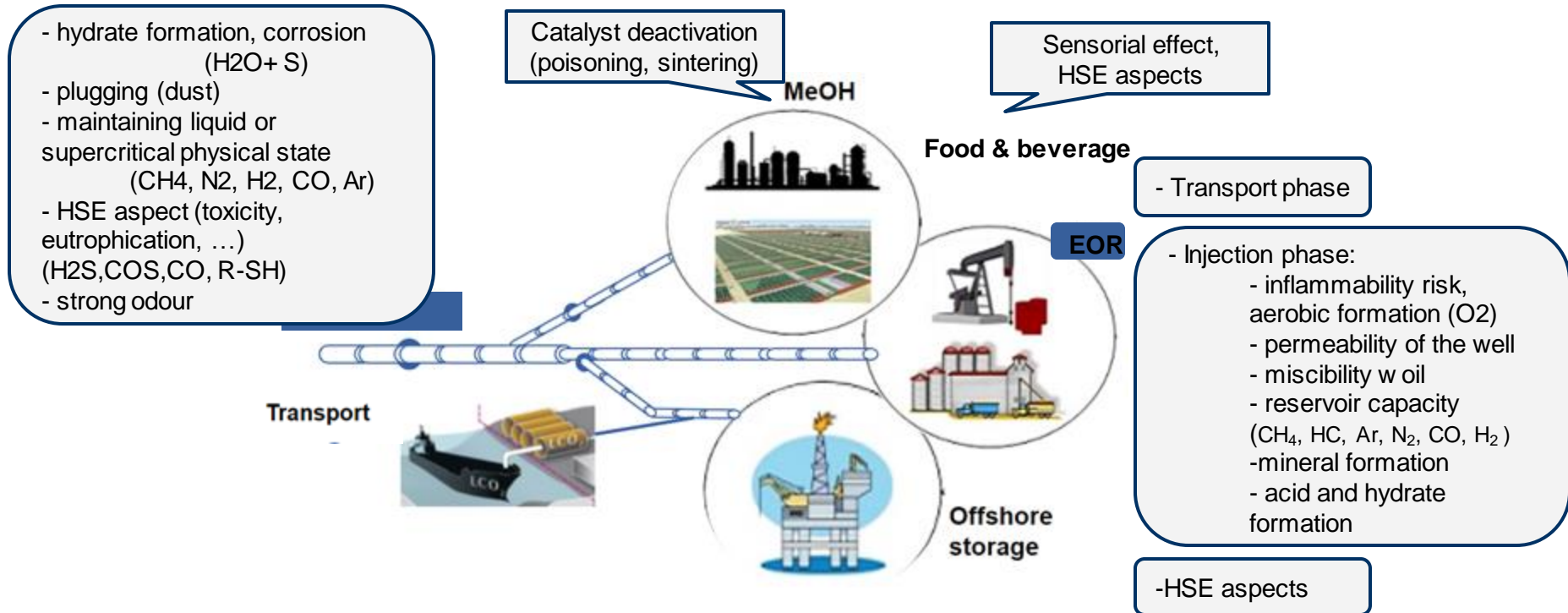


Offshore storage



Enhanced Oil Recovery

# Specifications designed by the transport and CO<sub>2</sub> usage





# Metrological challenges

# Key challenge : Raw gas composition ?

Compositions, variability vs feedstock, operation constraints



Steel

CO<sub>2</sub> SOURCE

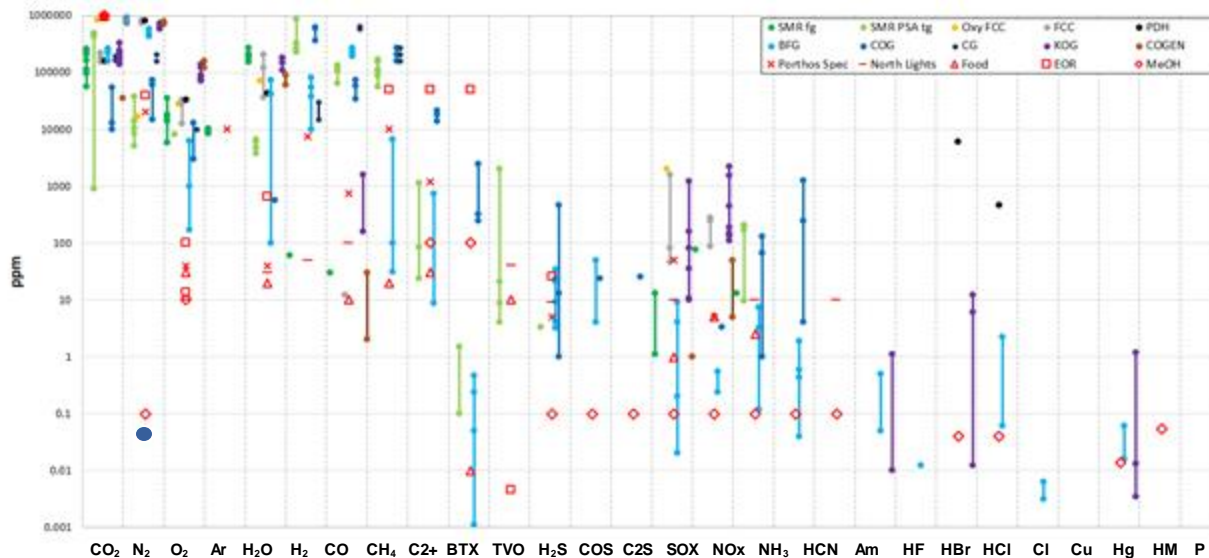


Power/  
Cement

Chemicals  
industries



H<sub>2</sub>  
Production



## ● How insure the reliability of the analytical results ?

- *Need reliable analytical techniques*
- *Need reference gas mixtures in CO<sub>2</sub> matrix*
- *Need sampling protocols adapted to the operation constraints (P, T, flow rate, gas composition) with compatible materials*

# Key challenges for process management

Fate of impurities in CO<sub>2</sub> separation process

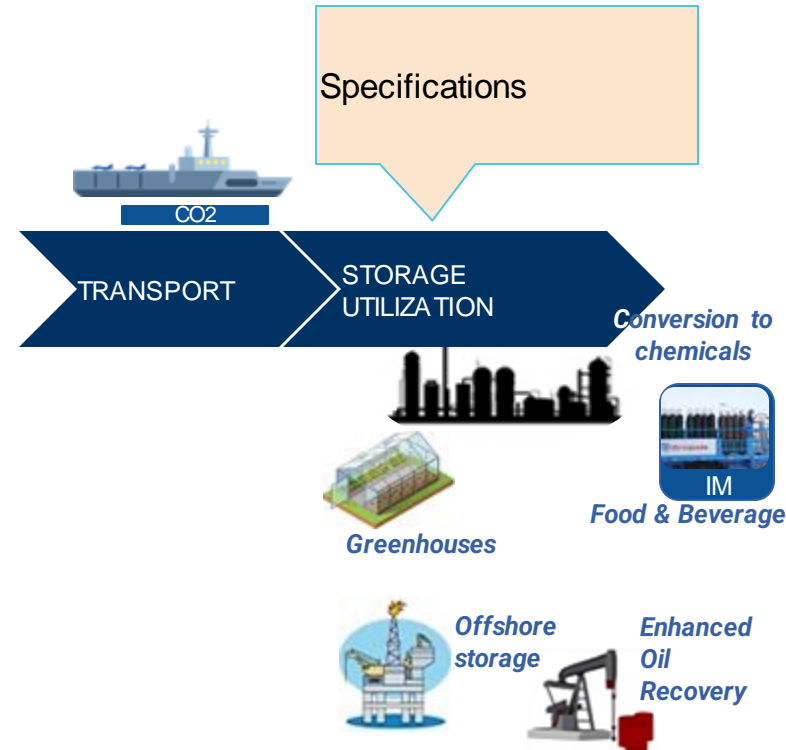


- Choice of the materials
- Risks of freezing
- Risks of plugging
- Recycles: prevent accumulation
- CO<sub>2</sub> removal: concentration phenomena

- **How insure the accuracy of the flow rate at each part of the process ?**
  - Need **primary flow standards** to enable calibration of flow meters for liquid and gaseous-phase of CO<sub>2</sub> with low uncertainties
  - Need **data verified models** to predict physical properties (e.g. phase equilibria, density and viscosity)
- **How insure the material compatibility with CO<sub>2</sub> and impurities?**
  - **Testing methods** to produce validated data for pipeline corrosion, material degradation
- **How control the impurities on line ?**
  - Need **validated sensors** and online analytical system
  - Need **reference gas mixtures** in CO<sub>2</sub> matrix

# Key challenges for transport , storage and utilisation

- **How measure CO<sub>2</sub> leaks at each step?**
  - *validation of systems capable of quantifying CO<sub>2</sub> leaks from pipelines, transport (e.g. shipping) or storage sites*
  - *Need data verified models to predict physical properties*
- **How insure the material compatibility with CO<sub>2</sub> and impurities in storage?**
  - *Testing methods to produce validated data for corrosion or chemical reactions*
- **How insure the quality of CO<sub>2</sub> for utilisation**
  - *develop methods for CO<sub>2</sub> purity analysis (ISO/TR 27921 or ISBT)*
  - *Need reference gas mixtures in CO<sub>2</sub> matrix*



- *MetCCUS: a project addressing industrial challenges*

<b>WP 1</b>	- metrology infrastructure for monitoring the <b>CO<sub>2</sub> gas flow</b> and <b>CO<sub>2</sub> liquid flow</b>
<b>WP 2</b>	- the meteorological support to enable the <b>measurement</b> and reporting of <b>emissions</b> to air during CCUS (capture process, infrastructure [leaks], geological storage)
<b>WP 3</b>	- new standards and analytical methods to perform gas composition measurement for CO <sub>2</sub> within CCUS ( <b>Reference materials</b> , sampling methods for representative sampling of key impurities, <b>online impurity analysis</b> )
<b>WP 4</b>	Study and model the <b>thermophysical properties</b> of CO <sub>2</sub> (mainly <b>liquid CO<sub>2</sub></b> ) to support the design, monitoring and maintenance of industrial infrastructures for CCUS

- *But only the first step: Need to address other challenges: raw gas analysis, on line control...*



# Thank you



# Dew-Point Measurements for Water in Compressed Carbon Dioxide

Christopher Meyer

Thermodynamic Metrology Group  
Physical Measurements Laboratory  
National Institute of Standards and Technology, USA

*MetCCUS Seminar on Metrology Support  
for Carbon Capture, Utilization and Storage*

*October 26, 2023*

# Working with

Allan Harvey

*Applied Chemicals and Materials Division*

*NIST*

*Boulder CO, USA*

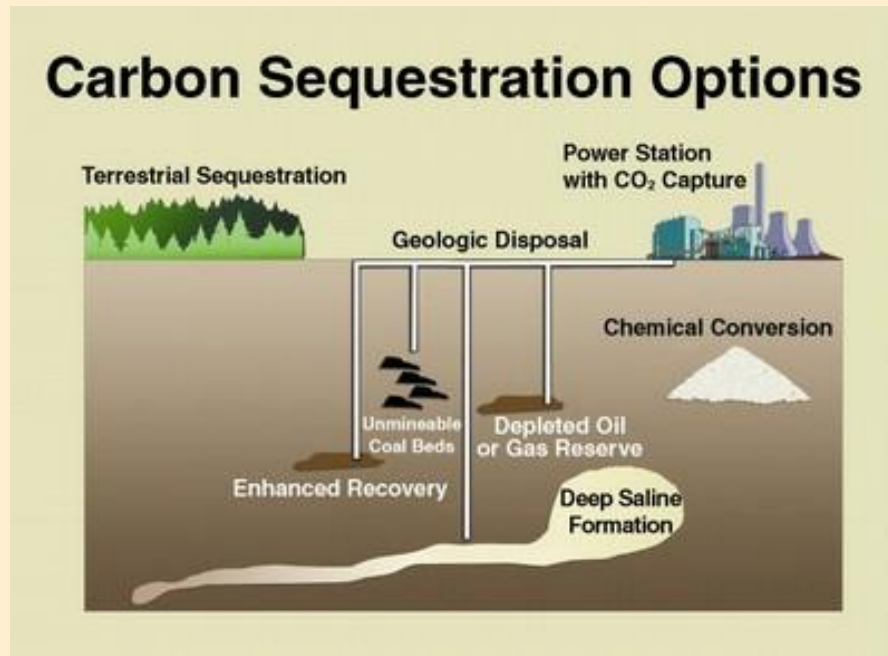
Paper published in AIChE Journal

C.W. Meyer and A.H. Harvey, “Dew-point Measurements for Water in Compressed Carbon Dioxide”, AIChE J. 61, 2913 – 2925, (2015).

# Carbon Capture, Utilization and Storage

Principle :

- 1) Flue gases are captured after coal is burned
- 2) CO<sub>2</sub> is separated from other flue gases
- 3) CO<sub>2</sub> is stored deep inside the earth at high pressures
  - a. in depleted oil or gas reserves
  - b. in unmineable coal beds
  - c. In saline aquifers



# Importance of removing H<sub>2</sub>O from humid CO<sub>2</sub>

- 1) Moisture can rust steel pipes
- 2) Compression of moist CO<sub>2</sub> requires more energy

Designing CO<sub>2</sub> capture systems requires accurate knowledge of dew point in CO<sub>2</sub> as function of mole fraction and pressure.

Accurate knowledge of  $T_{DP}(x,P)$  could save CCUS process as much as 300M/yr.

# Determining the CO<sub>2</sub> Dew-point Relations

$$x_w = \frac{e_w(T_{DP})}{P} f(T_{DP}, P)$$

$x_w$ : water amount (mole) fraction

$T_{DP}$ : dew point temperature

$e_w(T_{DP})$ : saturated water vapor pressure at  $T_{DP}$  (gas independent)

$P$ : pressure

$f(T_{DP}, P)$ : water vapor enhancement factor (gas dependent)

$e_w(T_{DP})$  is known

$f(T_{DP}, P)$  needs to be determined

# Facility for determining $f(T_{DP}, P)$

- 1) Saturation system for compressed CO<sub>2</sub>  
(generates unknown  $x$  using  $P$  and  $T_{DP}$ )
- 2) Gravimetric hygrometer (measures  $x_w$ )

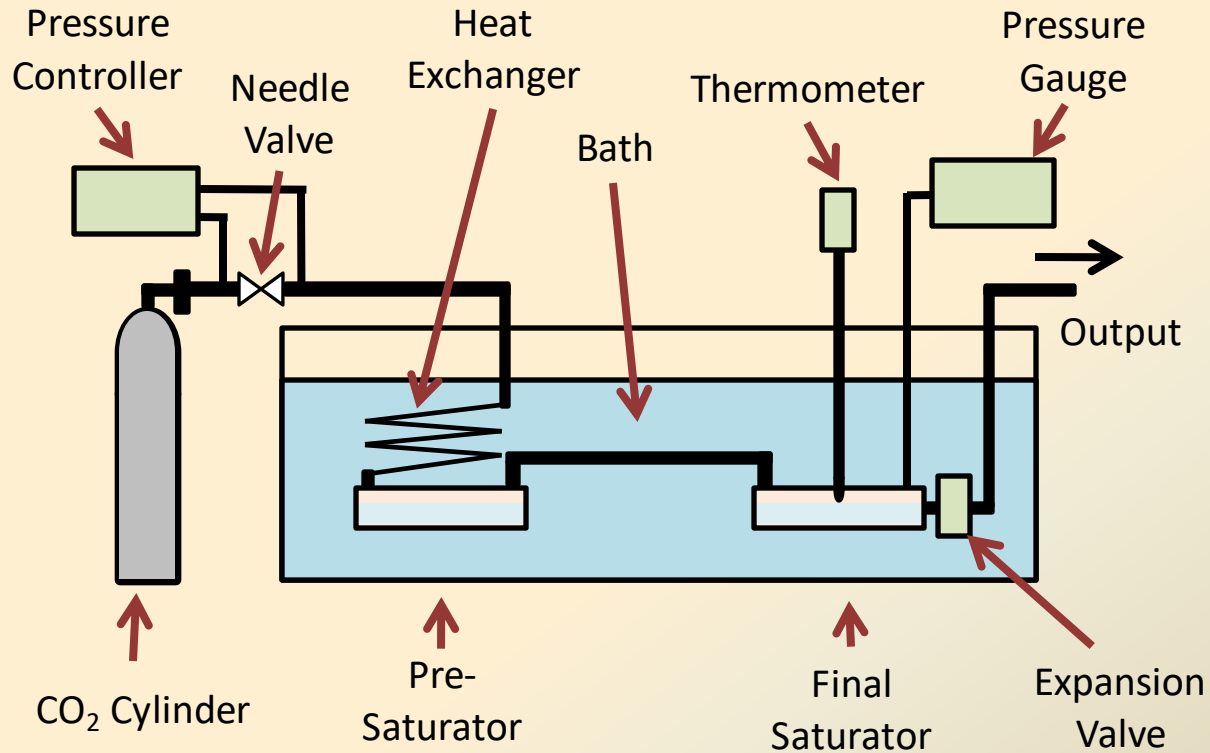
$$x_w = \frac{e_w(T_{DP})}{P} f(T_{DP}, P)$$

# Saturation System for Compressed CO<sub>2</sub>

Features:

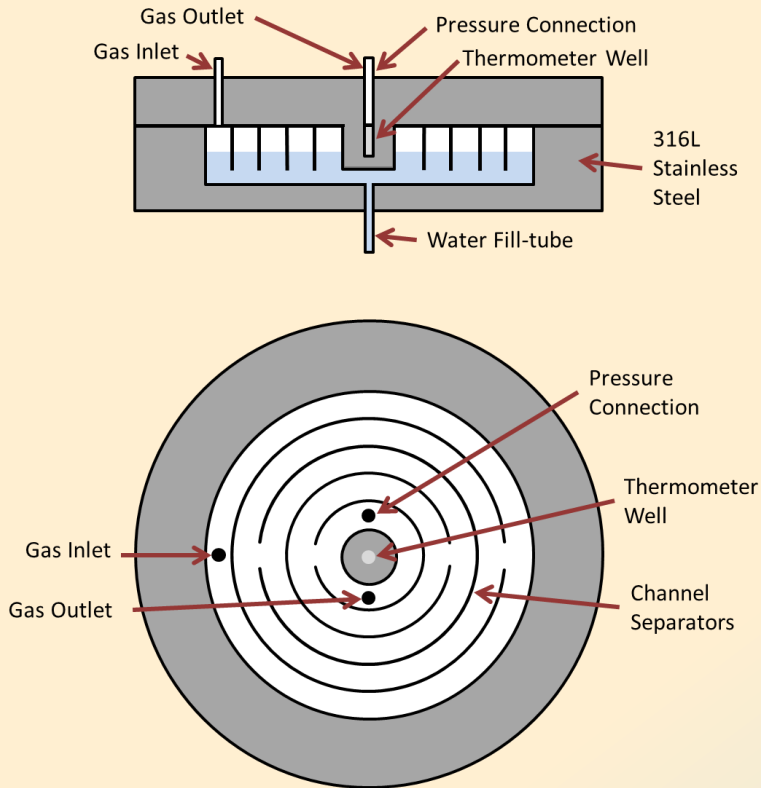
- 1) Saturates CO<sub>2</sub> completely
- 2) Operates at pressures up to 7 MPa
- 3) Allows frequent changes of water in saturator (CO<sub>2</sub> can react with water to make carbonic acid, but process is slow).

# Design for Saturation System





# Design for Saturator



# NIST Gravimetric Hygrometer

Provides a primary method of humidity measurement giving water amount fraction  $x_w$ :

$$x_w = \frac{m_w/M_w}{m_w/M_w + m_g/M_g}$$

$m_w$ : mass of water vapor

$m_g$ : mass of carrier gas

$M_w$ : molecular weight of water vapor

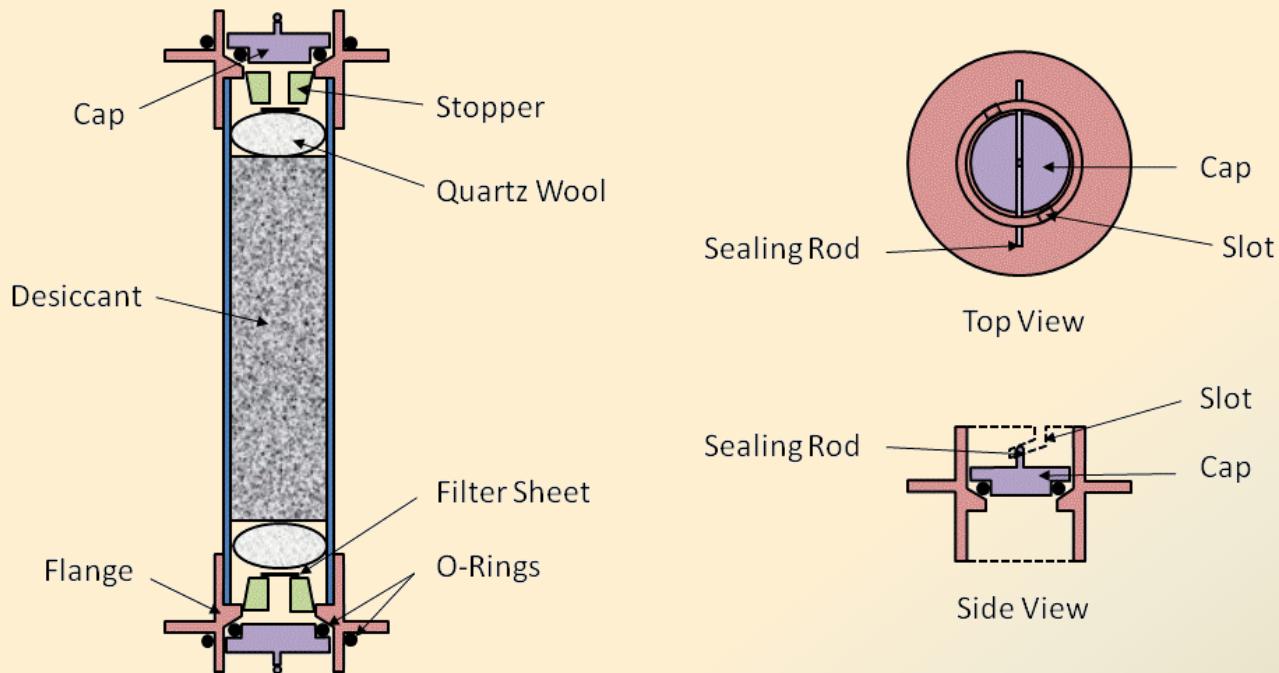
$M_g$ : molecular weight of carrier gas

Principle of Operation:

- 1) Separates moisture from dry gas using desiccants
- 2) Determine  $m_w$  by measuring increase in mass of water collection tubes
- 3) Determine  $m_g$  using volume, temperature and pressure measurements and using equation of state

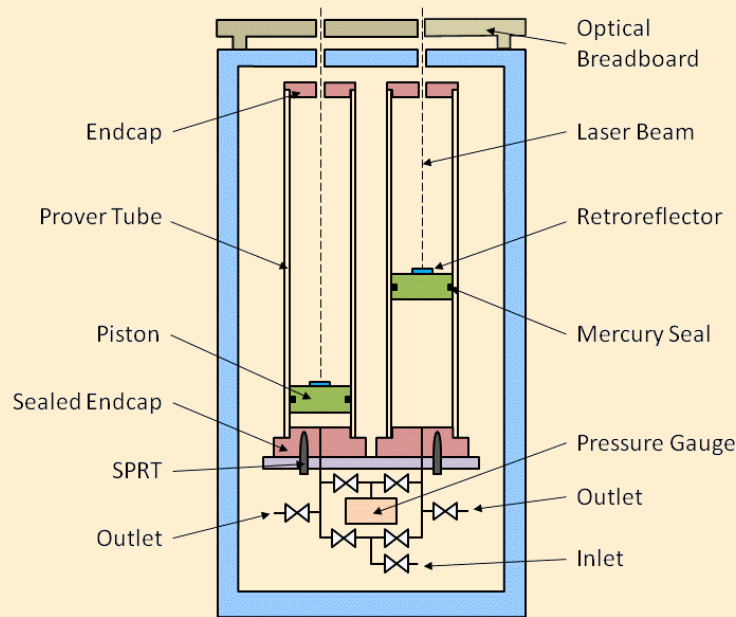
Relative Uncertainty of amount fraction measurements using Gravimetric Hygrometer: 0.1%

# Water Collection Tubes



- Desiccant used: Magnesium Perchlorate
- Mass measurements made before and after water collection using electronic balance that compares tube mass to standard mass.
- Three tubes used in series. Most all water collected in 1<sup>st</sup> tube.

# Prover Tube Gas Collection System

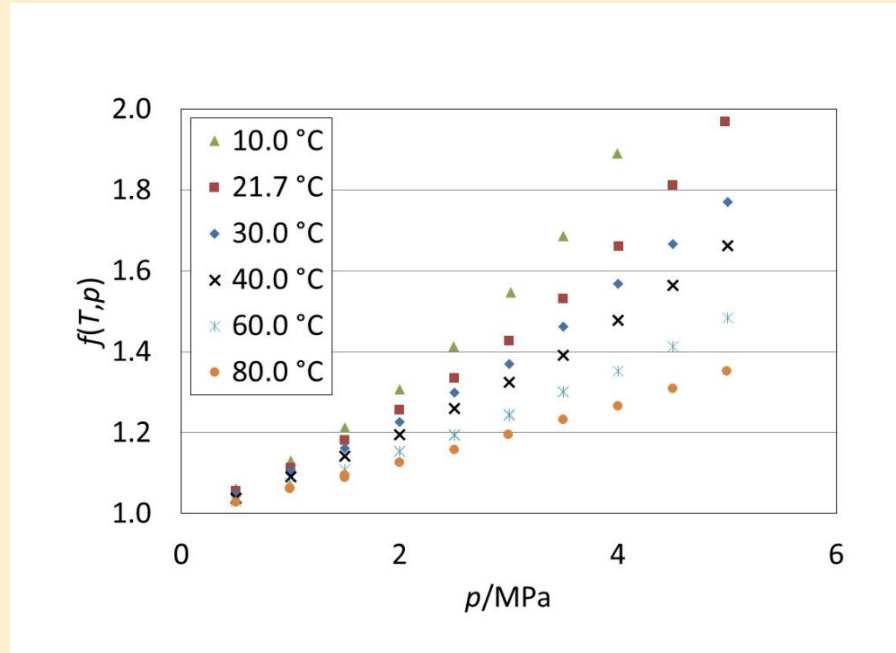


- Laser interferometer measures piston displacement to determine gas volume
- Pressure and temperature measurements determine gas density
- Gas mass under piston calculated from volume and density
- Alternating pistons allow continuous gas flow
- Prover tube collects gas underneath piston

# Measurement Plan

- 1) Perform measurements on 6 isotherms between 10 °C and 80 °C
- 2) Perform measurements from 0.5 MPa to 5 MPa in 0.5 MPa increments
- 3) Pressure range limited by
  - a) CO<sub>2</sub> sat. vapor pressure at ambient temperature
  - b) CO<sub>2</sub> hydrates (high pressures at low temperatures)

# Water-vapor Enhancement Factor in CO<sub>2</sub>

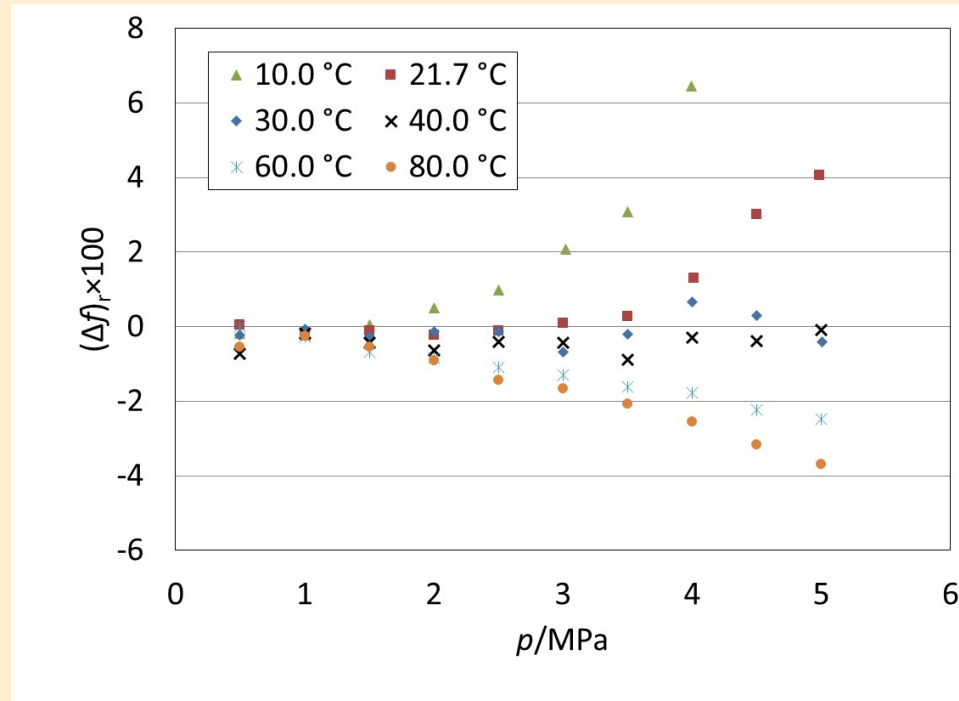


Note:

- 1)  $f$  increases monotonically with pressure
- 2)  $f$  decreases monotonically with temperature
- 3) Over range studied,  $f$  varies from 1 to 2.
- 4) Difference between  $f=1$  and  $f=2$  corresponds to a dew point change of 9.5 °C. (for constant  $x_w$ , higher  $f$  means lower  $T_{DP}$ ).

# Comparison with Theoretical Results

$$(\Delta f)_r = [f(\text{measured}) - f(\text{calculated})] / f(\text{calculated})$$



Theoretical Results:

$f$  calculated using interaction second virial coefficient  $B_{12}$  values of

R. J. Wheatley and A. H. Harvey, *J. Chem. Phys.* **134**, 134309 (2011).

Conclusion:  $C_{112}$  and  $C_{122}$  values must also be considered!

$$\frac{p}{\rho RT} = 1 + B\rho + C\rho^2 + \dots$$

$$B = x_1^2 B_{11} + 2x_1 x_2 B_{12} + x_2^2 B_{22}$$

$x_1$ : CO<sub>2</sub> amount fraction

$x_2$ : H<sub>2</sub>O amount fraction

$B_{11}$ : CO<sub>2</sub> 2<sup>nd</sup> virial coeff.

$B_{22}$ : H<sub>2</sub>O 2<sup>nd</sup> virial coeff.

$B_{12}$ : CO<sub>2</sub>/H<sub>2</sub>O interaction 2<sup>nd</sup> virial coeff.

# $C_{112}$ and $C_{122}$ considered

$$\frac{p}{\rho RT} = 1 + B\rho + C\rho^2 + \dots$$

$$C = x_1^3 C_{111} + 3x_1^2 x_2 C_{112} + 3x_1 x_2^2 C_{122} + x_2^3 C_{222}$$

$x_1$ : CO<sub>2</sub> amount fraction

$x_2$ : H<sub>2</sub>O amount fraction

$C_{11}$ : CO<sub>2</sub> 3<sup>rd</sup> virial coeff.

$C_{22}$ : H<sub>2</sub>O 3<sup>rd</sup> virial coeff.

$C_{112}$ : CO<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O interaction 3<sup>rd</sup> virial coeff.

$C_{122}$ : CO<sub>2</sub>/H<sub>2</sub>O/H<sub>2</sub>O interaction 3<sup>rd</sup> virial coeff

Best-fit values of  $C_{122}$  used

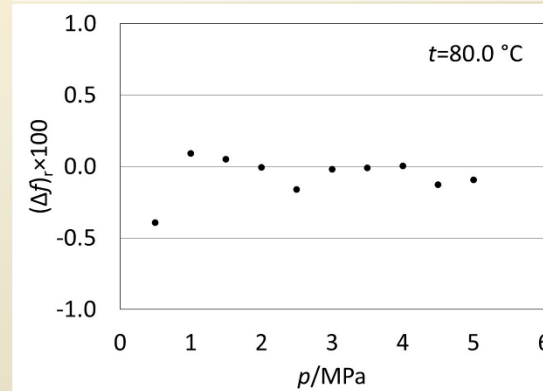
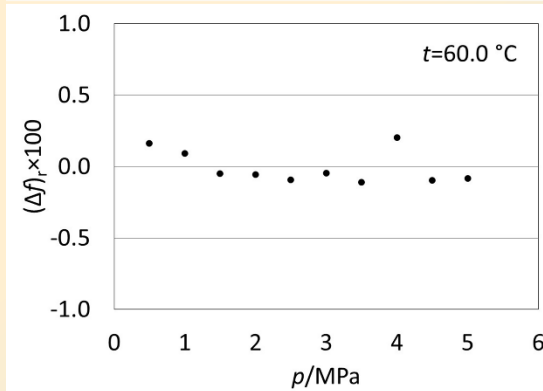
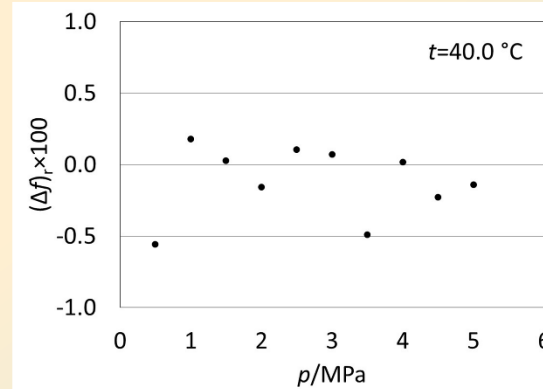
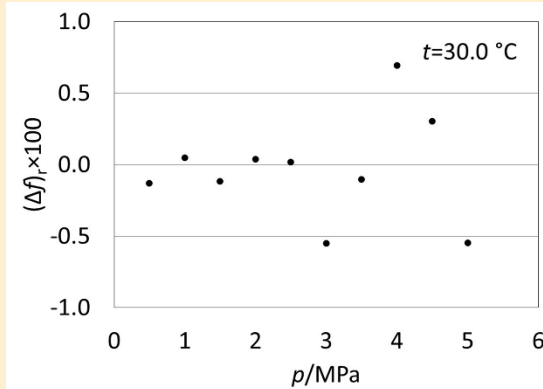
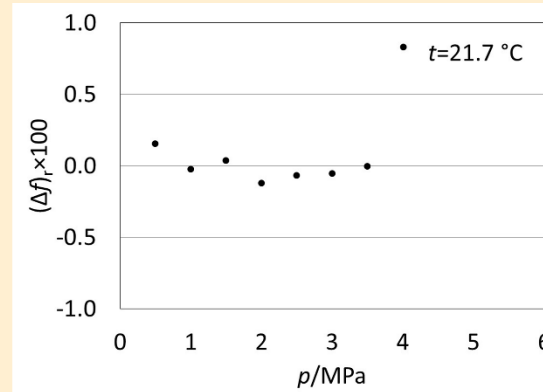
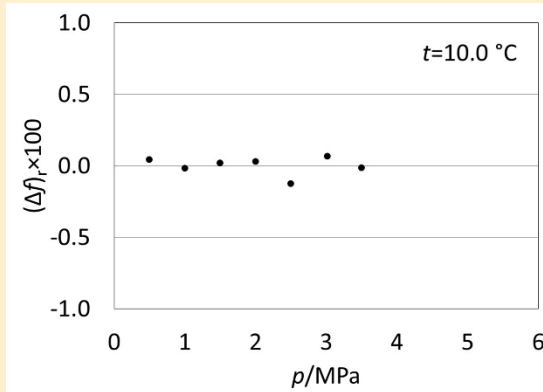
Theoretical values of  $C_{122}$  used



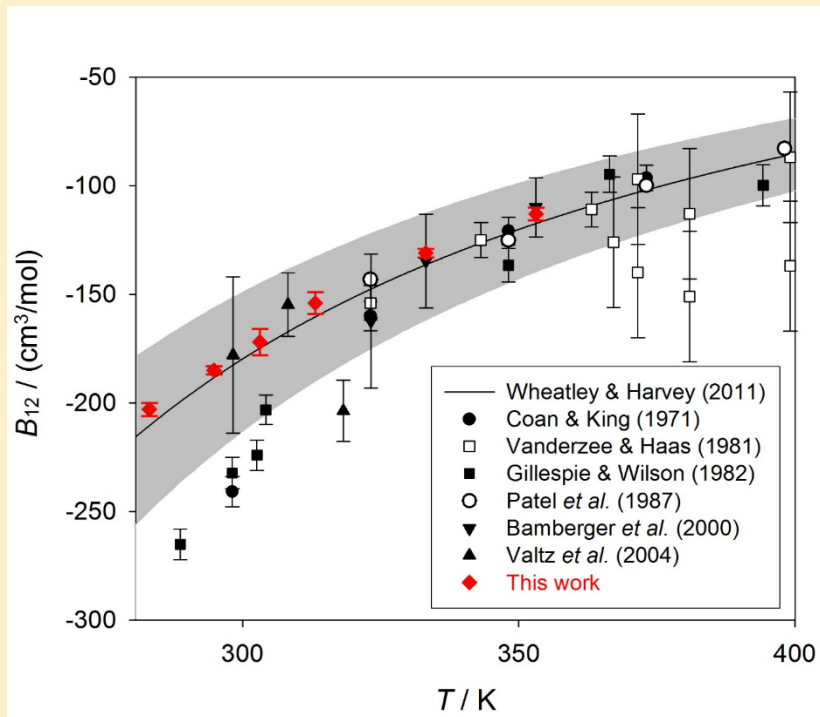
# Comparison with Theoretical Results

Theoretical Results:

$f$  calculated using best-fit values of  $B_{12}$  and  $C_{112}$ .



# Water-CO<sub>2</sub> Cross Second Virial Coefficient



Temp, K	Wheatley and Harvey	Meyer
283	-210 ± 40	-203 ± 3
295	-188 ± 35	-186 ± 2
303	-175 ± 30	-173 ± 6
313	-160 ± 27	-155 ± 5
323	-136 ± 23	-132 ± 2
343	-117 ± 20	-113 ± 3

# Conclusion

- Carbon Capture, Utilization and Storage (CCUS) has the potential of greatly reducing emissions of CO<sub>2</sub> from power plants into the atmosphere.
- Water-vapor enhancement factor is an important thermophysical property for CCUS
- Facility constructed for measuring the water-vapor enhancement factor; facility uses humidity generator that saturates CO<sub>2</sub> with water at pressures up to 5 MPa
- Measurements made on 6 isotherms; measurements in good agreement with theoretical predictions of Wheatley and Harvey but with much less uncertainty

# METCCUS

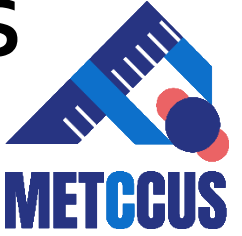
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## SAMPLING OF CO<sub>2</sub> FOR PURITY ASSESSMENT: METHODS AND CHALLENGES

*Karine Arrhenius, RISE*



# SAMPLING OF CO<sub>2</sub> FOR PURITY ASSESSMENT: METHODS AND CHALLENGES



- Introduction
- Challenges
- Vessels
- Considerations
- Material compatibility

# INTRODUCTION

- Due to the production methods or the origin of the carbon dioxide, it usually contains species in traces that can have a negative impact on the equipment they come into contact with
- Several standards contain requirements for CO<sub>2</sub> quality assessment for different applications
- These standards requires often analysis in a laboratory and therefore requires the collection and transport of a gas sample from the point of use
- The sample taken must be **representative** of the gas supplied; this assumes that no compounds are added to or removed from the gas during sampling



# CHALLENGES

The main challenge is for species at trace levels for which the risk of loss of contaminants in the vessels and sampling lines must be taken into consideration

- ❑ partial adsorption or irreversible adsorption
- ❑ reaction (chemical reaction between species or between species and the matrix)

Other challenges arise from the need for flow measurement specifically for the enrichment methods, the exact composition of which may not be known until it has been fully analysed in a laboratory.

Important challenges arise from the physical properties of  $\text{CO}_2$  itself. The critical point of pure  $\text{CO}_2$  is close to the ambient temperature. Therefore, phase changes and multiphase conditions can occur at the sampling points. There may be a partitioning of species between the different phases, and if only the gas phase is analysed, the composition may be underestimated



# VESSELS

Gas cylinders

Canisters

Sampling bags

Impingers

Sorbents



No enrichment

Enrichment



# DIFFERENT CONSIDERATIONS

## THE CONDITIONS AT THE SAMPLING POINT MUST FIT THE REQUIREMENT FOR THE VESSELS



- Pressure: if the pressure at the sampling point is low (less than 1 bar), it would be difficult to fill a cylinder for example. If the pressure is high (>3 bar), a reduction is needed for sorbents, impingers and bags
- Temperature: Bags, sorbents.. have max. operating temperature
- Flow: needs to be controlled for some vessels such as sorbent tubes and limited (for example 0.5 l/min)
- Gas permeability (mostly for bags)

- Enough volume sampled to perform all analyses (all replicates) and all instruments
- Enough pressure if needed by the instruments, pressure from the vessels may need to be reduced
- Adequate temperature, many instruments work at ambient temperatures



## THE REQUIREMENT FOR THE VESSELS MUST FIT THE CONDITIONS OF THE ANALYTICAL INSTRUMENTS

# MATERIAL COMPATIBILITY



Materials in contact with gases that may contain reactive impurities should be impermeable to all species and should have a minimum of sorption and chemical inertness to the constituents being sampled.

The same considerations apply to all parts of the sampling line and especially to those parts where pressure reduction takes place

Material compatibility issues are often not well demonstrated experimentally, it is of great importance to increase the knowledge of adsorption effects of relevant species on different materials under relevant conditions (matrix, pressure, concentration)

Need for systematic recovery experiments and short-term stabilities at defined and relevant conditions in terms of pressure, matrix and concentration

The results of these investigations should be compiled in material compatibility tables to assist industry in selecting suitable materials for vessels and sampling lines.

# TESTS PERFORMED DURING METCCUS: VESSELS



## TRUE BLUE

From Airborne labs

Specifically designed for CO<sub>2</sub> sampling

Proprietary multi-layer barrier film



## CALI5BOND

From Calibrated Instruments inc.

Multi layer foil Sampling Bags



## MULTIFOIL

From Restek

Multi layer foil Sampling Bags



## ALTEF

From Restek

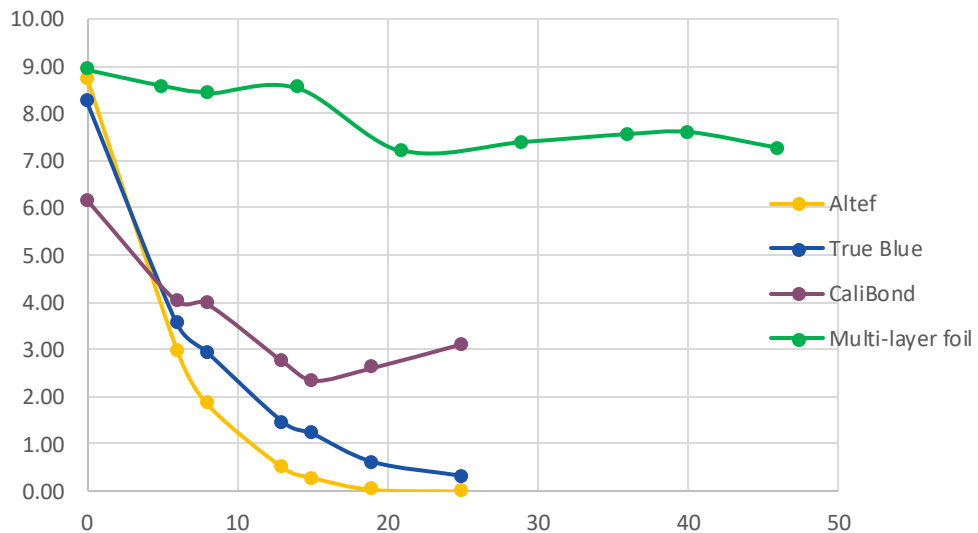
Polyvinylidene fluoride (PVDF) film, alternative to Tedlar



# TESTS PERFORMED DURING METCCUS: RESULTS



6-8 ppm methanol in CO<sub>2</sub>



Methanol Limit required: 10  $\mu\text{mol/mol}$   
(beverage, EIGA 70/17)

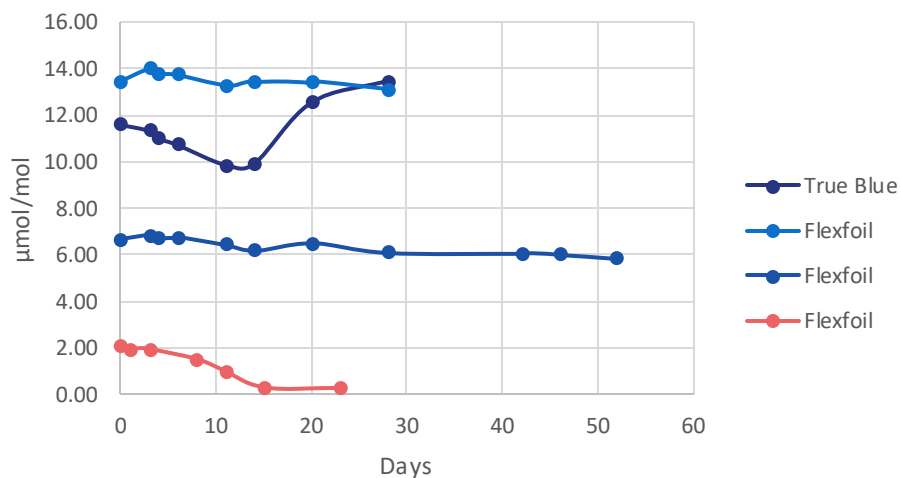
Bags	concentration	Stability	Comments
True Blue	8.6	Red	
Multi-layer foil	9.0	Green	
Cali5Bond	6.1	Yellow	
Altef	9.0	Red	

# TESTS PERFORMED DURING METCCUS: RESULTS



Acetaldehyde. Limit required: 0.2  $\mu\text{mol/mol}$ ,  
(beverage, EIGA 70/17)

Acetaldehyde in CO<sub>2</sub>



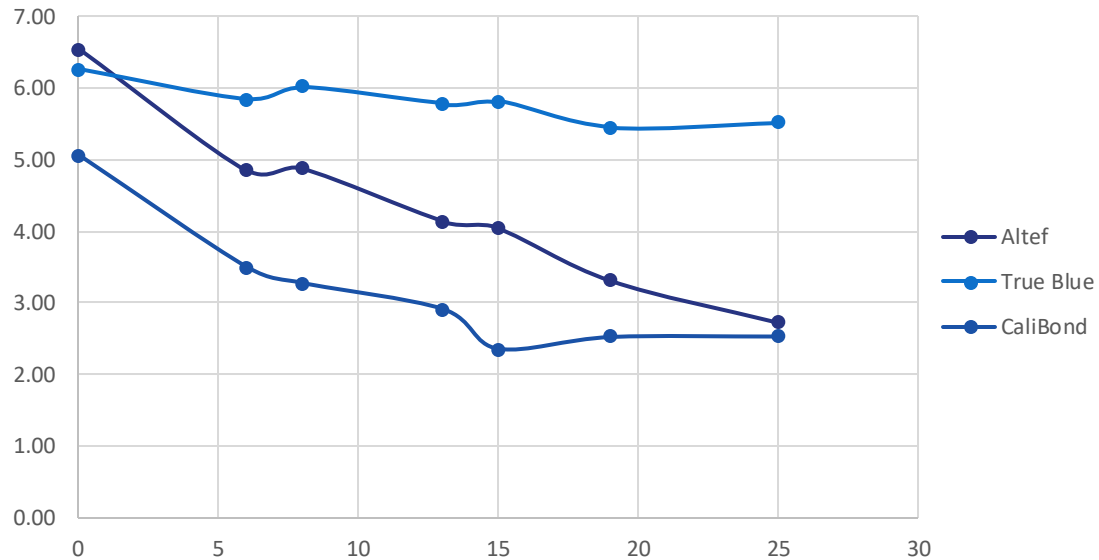
Bags	concentration	Stability	Comments
True Blue	12		Bag not enough filled, acetaldehyde in blank
Multifoil	14		Bag not enough filled, acetaldehyde in blank
Multifoil	7		Acetaldehyde in blank
Multifoil	2		Bag not enough filled, acetaldehyde in blank

# TESTS PERFORMED DURING METCCUS: RESULTS



6-8 ppm ethanol in CO2

Ethanol Limit required: ?  $\mu\text{mol/mol}$

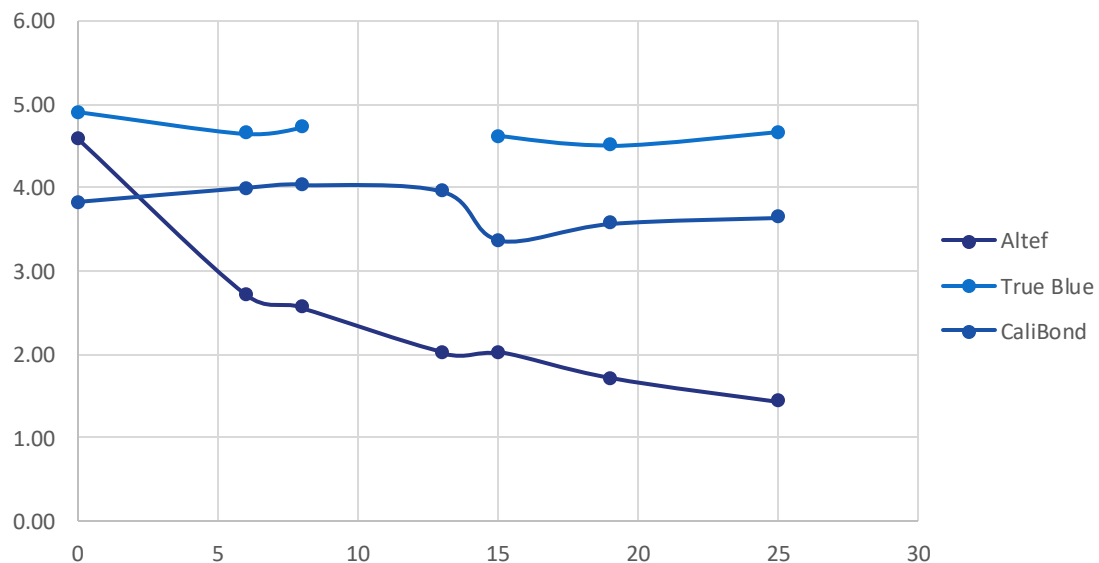


Bags	concentration	Stability	Comments
True Blue	6.3		
Multi-layer foil	-		
Cali5Bond	5.0		
Altef	6.5		

# TESTS PERFORMED DURING METCCUS: RESULTS



6-8 ppm acetone in CO2



Acetone Limit required: ?  $\mu\text{mol/mol}$

Bags	concentration	Stability	Comments
True Blue	4.9		
Multi-layer foil	-		
Cali5Bond	3.9		
Altef	4.7		

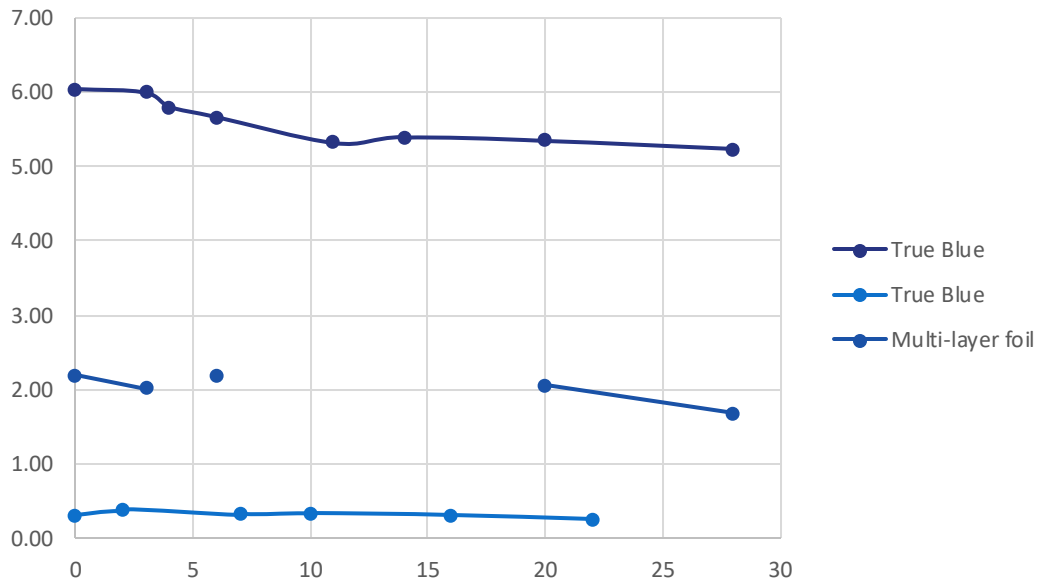
# TESTS PERFORMED DURING METCCUS: RESULTS



Not appropriate for benzene



Benzene in CO<sub>2</sub>



Benzene Limit required: 0.02  $\mu\text{mol/mol}$

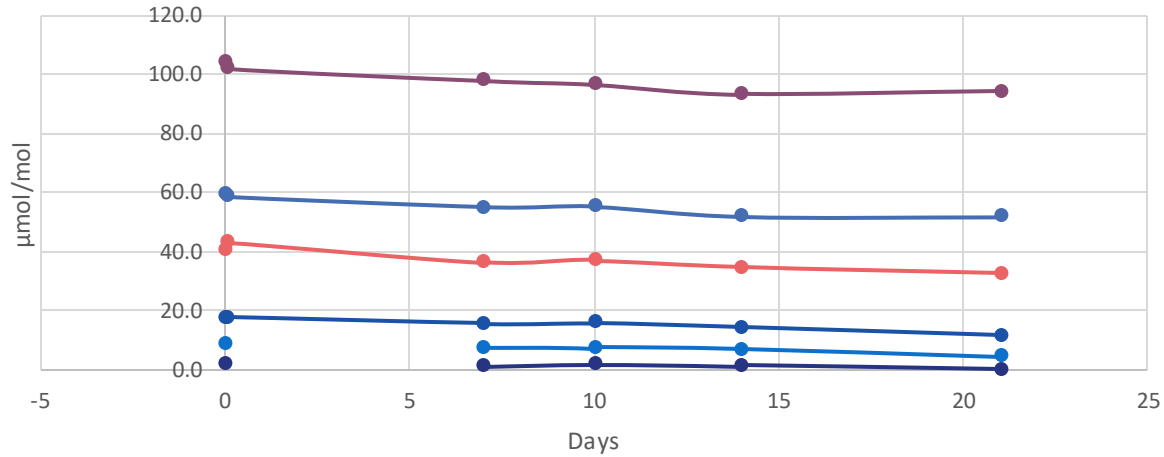
Bags	concentration	Stability	Comments
True Blue	6.0		
True Blue	0.3		
Multi-layer foil	3.9		Stable but value lower at D0 (3.6 $\mu\text{mol/mol}$ )



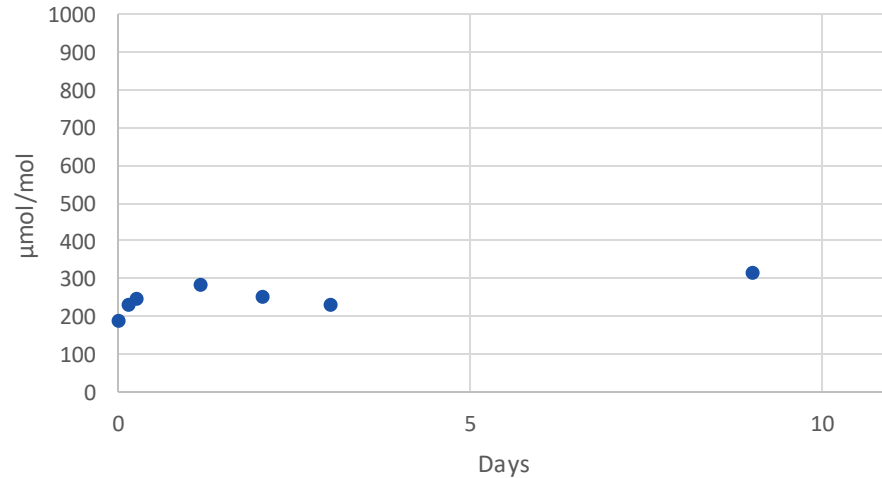
# TESTS PERFORMED DURING METCCUS: RESULTS



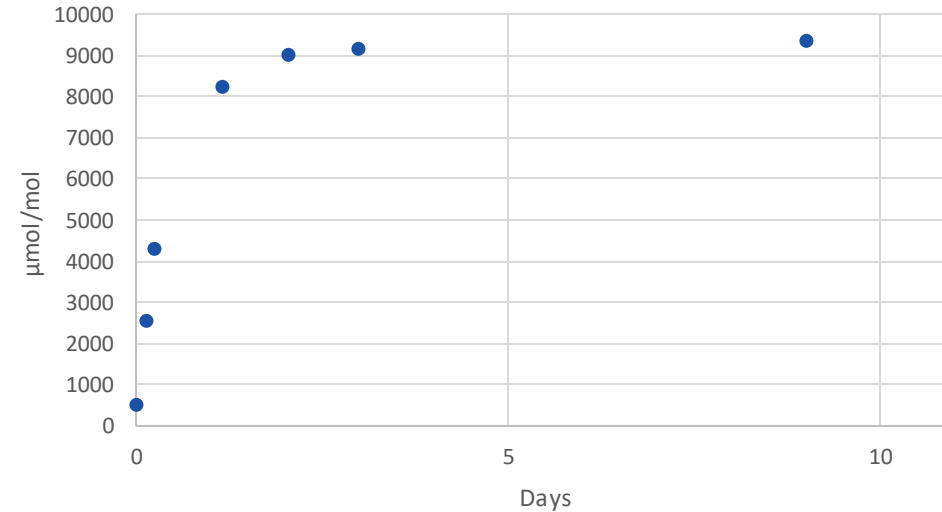
H<sub>2</sub>S in CO<sub>2</sub>



Permeability of oxygen



Permeability for water



# TESTS PERFORMED DURING METCCUS: SUMMARY

Bags	Methanol	Ethanol	Acetone	Benzene	Hydrogen sulphide	Acetaldehyde
True Blue	Red	Green	Green	Green	Grey	Green
Cali5Bond	Red	Red	Green	Red	Green	Grey
Restek Multi-layer foil	Green	Grey	Grey	Red	Grey	Green
Restek Altef	Red	Red	Red	Grey	Grey	Grey

More tests to be performed:

- H<sub>2</sub>S in True Blue and restek multifoil
- Acetaldehyde and benzene at lower concentrations
- Ethanol and acetone in Restek multilayer

# CONCLUSIONS



- The overall conclusion is that no single bag is suitable for sampling all the impurities present in CO<sub>2</sub>. A combination of vessels is likely to be required to cover the wide range of impurities which have a wide range of boiling points, polarities, water solubilities, and reactivities
- Best results for True Blue (except for methanol) and potentially for Restek multilayer which is suitable for methanol
- Results highlight the needs to perform stability studies in relevant conditions
- Other studies of interest not planned: Influence of combined impurities

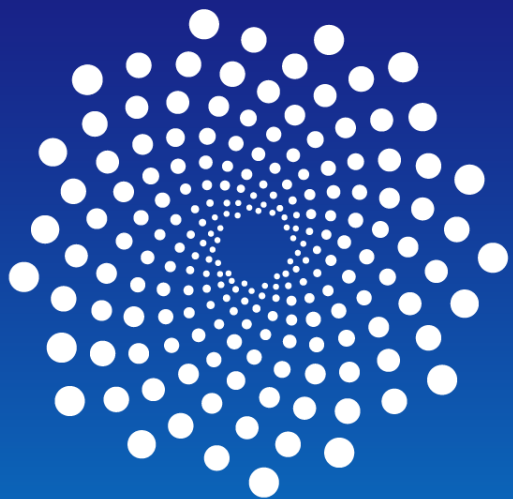


# THANK YOU!



[KARINE.ARRHENIUS@RI.SE](mailto:KARINE.ARRHENIUS@RI.SE)





**VSL**

**National  
Metrology  
Institute**

## CCUS challenges

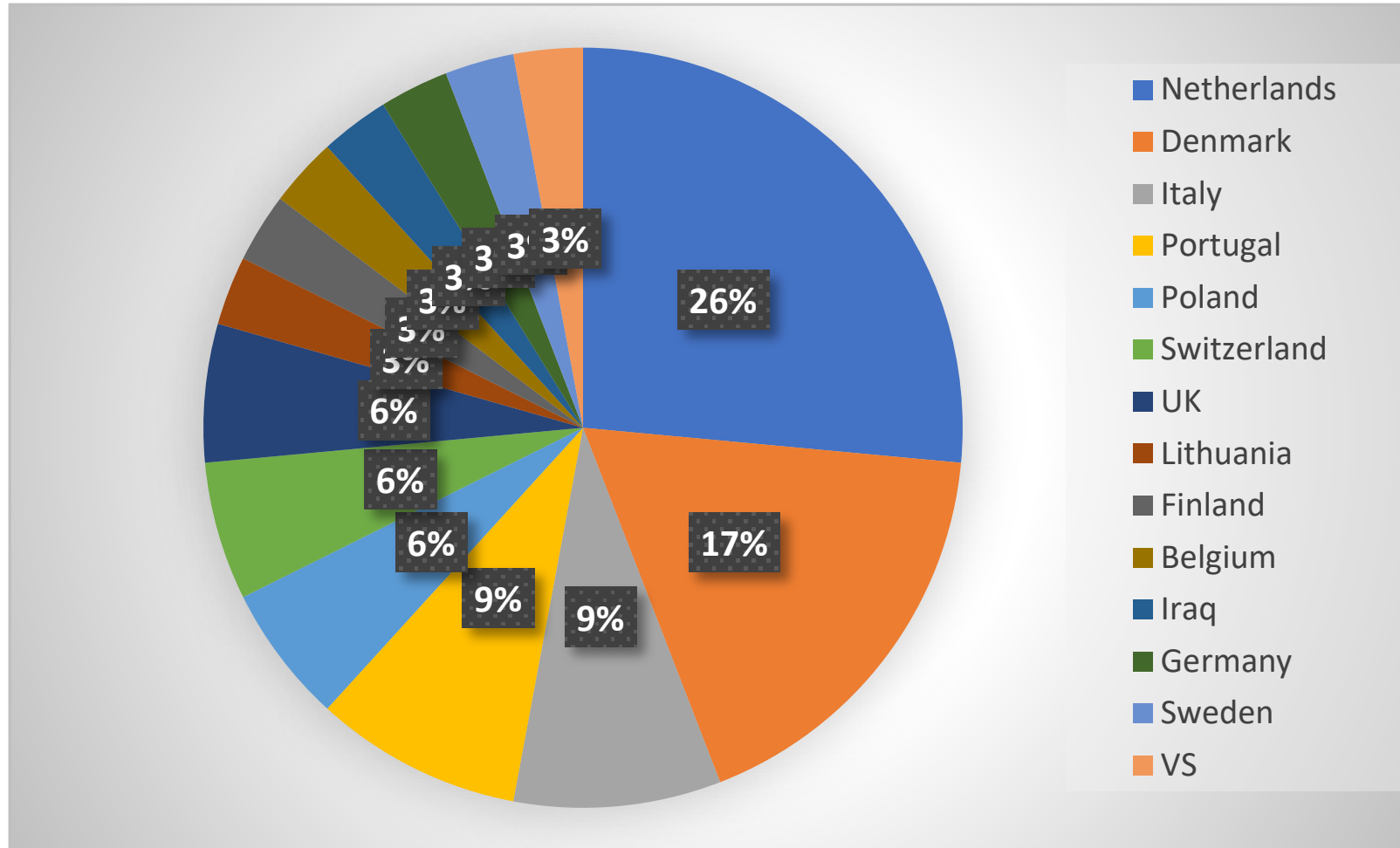
**Seminar Metrology Support for Carbon  
Capture Utilization and Storage**

**Iris de Krom**

**26 October 2023 – Online**



**METCCUS**



Note: this is based on a survey shared during the first 10 minutes of the seminar. People from other countries, including the Americas, joined later on.

# CCUS general challenges

- Organization of ring tests
- DAC - Direct Air Capture
- Tracing of the origin of CO<sub>2</sub>
- Standardization
- Unclear specifications for CO<sub>2</sub> and impurities
- Diversity of applications along the CCUS value chain
- Storage
- Legislation & Carbon accounting
- How much carbon do we need to capture ?
- How much captured carbon can be converted to fuels, chemicals and materials?
- How can we connect different CO<sub>2</sub> networks?

# CCUS measurement challenges

## Flow metering

- Ensuring accuracy of measurements across a wide flow range and CO<sub>2</sub> with variable purity
- Calibrated, accredited and accurate flow measurements for supercritical CO<sub>2</sub> flow with acceptable uncertainties
- Measuring for allocation
- Flow meters suitable for Fiscal Flow measurement traceable to SI
- Transferability of alternative fluid calibrations (i.e. Coriolis with water)

## Emission monitoring

- Amines break through products emissions
- SO<sub>3</sub> emissions
- Amines in flue gas – number of species and concentration levels.
- Pipeline leak detection
- Direct measurements of CO<sub>2</sub>, post capture



# CCUS measurement challenges

## Chemical metrology

- CO<sub>2</sub> traceable Standards/Reference gas mixtures
  - Amines, NO<sub>x</sub>, SO<sub>x</sub> (ppm level)
  - Metals such as Hg and Cd (ppb level)
  - Dust
- Reliable analytical techniques for online measurement of impurities
- Need sampling protocols adapted to the operation constraints (P, T, flow rate, gas composition) with compatible materials
- Raw gas analysis

## Physical properties

- Need data verified models to predict physical properties
- Thermodynamic state and gas properties after capture
- Equations of state, how will they be implemented in flow computers for fiscal metering?
- Accurate measurement and analysis of moisture in CO<sub>2</sub>

# Thank you for your attention

- Visit

- [www.metccus.eu](http://www.metccus.eu)
- [MetCCUS: Overview | LinkedIn](#)

- Contact

Project coordinator

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