DOE Contract DE-FE0012829

Pilot Test of a Nanoporous, Super-hydrophobic Membrane Contactor Process for Post-combustion CO_2 Capture

Shiguang Li, Travis Pyrzynski, Timothy Tamale, Riley Silber, Mark Fitzsimmons, James Aderhold, Howard Meyer, and John Marion, ***GTI***

Yong Ding, Uttam Shanbhag, and Ed Sanders, ***Air Liquide Advanced Separations (ALaS)***

U.S. Department of Energy
National Energy Technology Laboratory
Carbon Management and Natural Gas & Oil Research Project Review Meeting
Virtual Meetings, August 12, 2021

Project overview

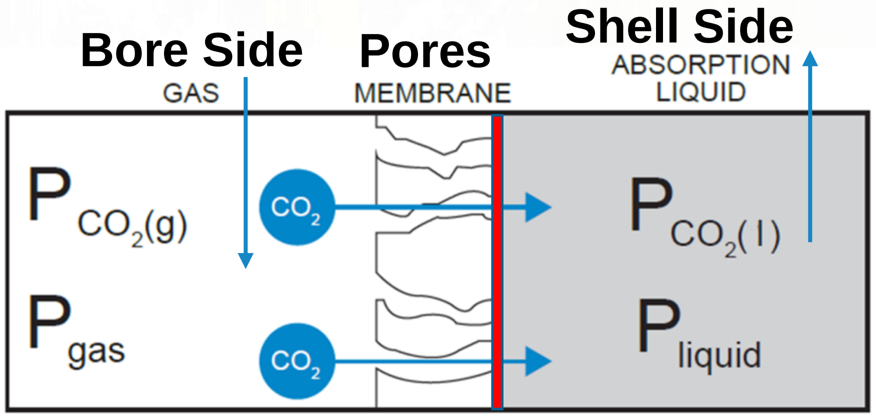
- **Performance period**: October 1, 2013 – June 30, 2022
- **Total funding**: \$15.6MM (DOE: \$12.5MM, Cost share: \$3.1MM)
- **Objectives**:
  - Build and operate a 0.5 MW_e pilot-scale CO_2 capture system and conduct tests on coal flue gas at the National Carbon Capture Center (NCCC)
  - Demonstrate a continuous, steady-state operation for ≥ 2 months
- **Goal:** Achieve DOE's goal of ≥95% CO_2 purity at a cost of ≤\$40/tonne of CO_2 captured by 2025
- **Team**:

Member	Roles
gti	• Project management and planning • Process design and testing
Air Liquide ALaS PoroGen PEEK	• Membrane and module development
Trimeric Corporation	• Techno-Economic Analyses (TEA)
NCCC	• Site host

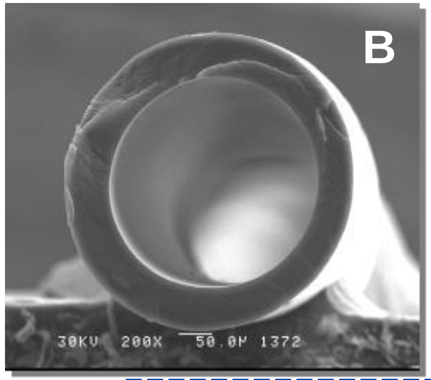
Hollow Fiber Membrane Contactor (HFMC) technology

HFMC: high surface area device that facilitates mass transfer

Centerline of bore – not to scale

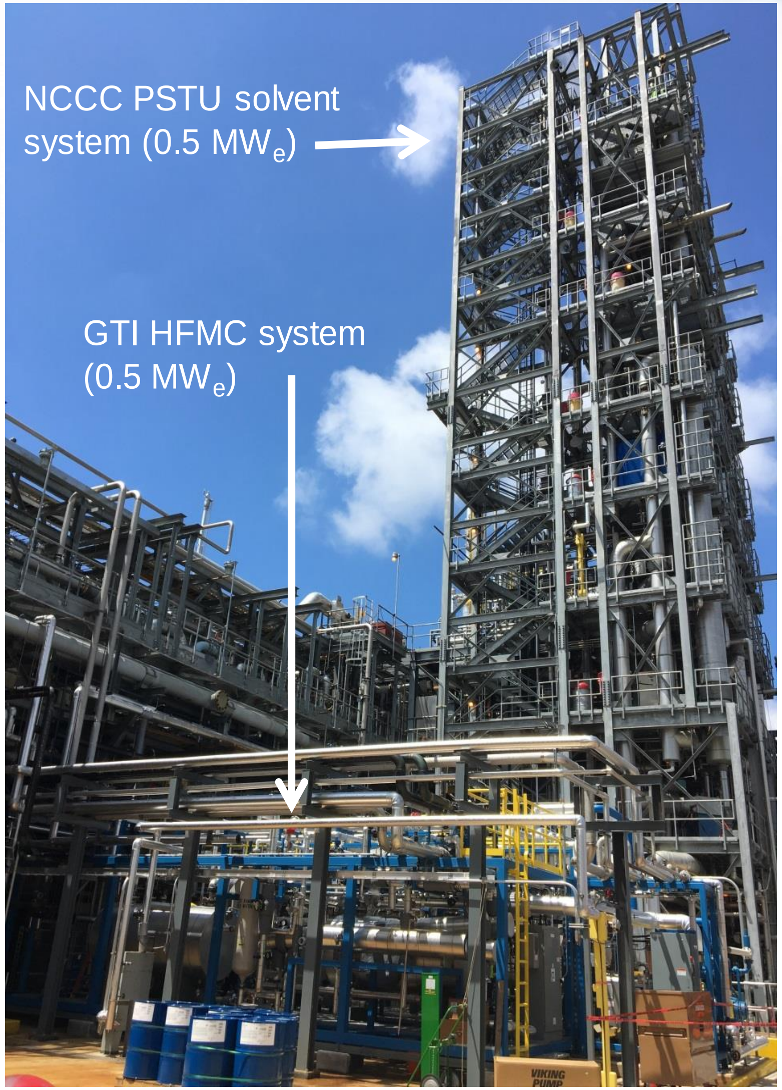


Hydrophobic coating layer to prevent wetting



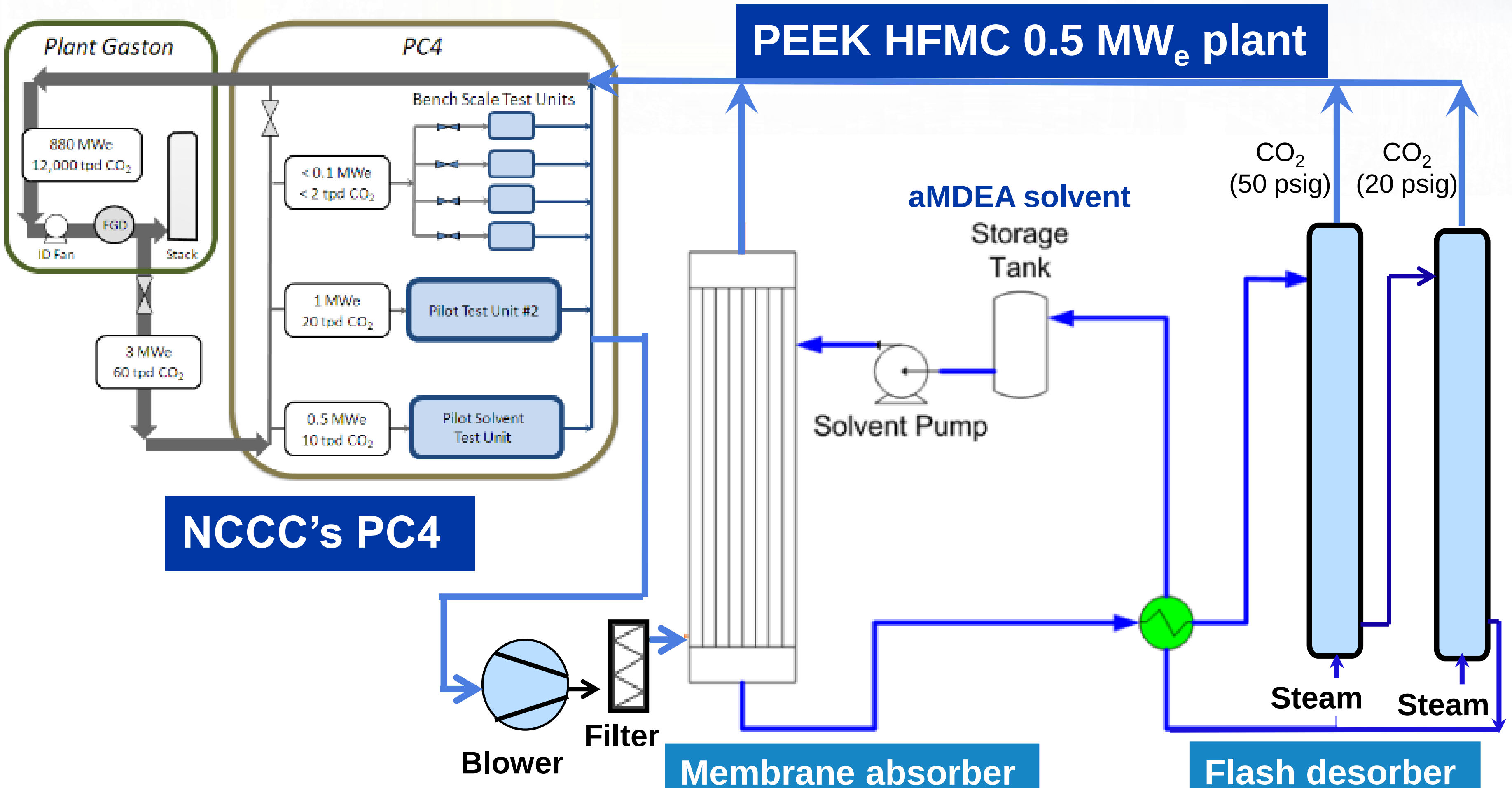
PEEK spun into high-packing density, hollow fibers

8-inch-diameter commercial cartridges with ~2,000 GPU intrinsic CO_2 permeance used in pilot scale testing



Pilot plant (10 ton/day) being tested at the National Carbon Capture Center (NCCC)

HFMC process at NCCC



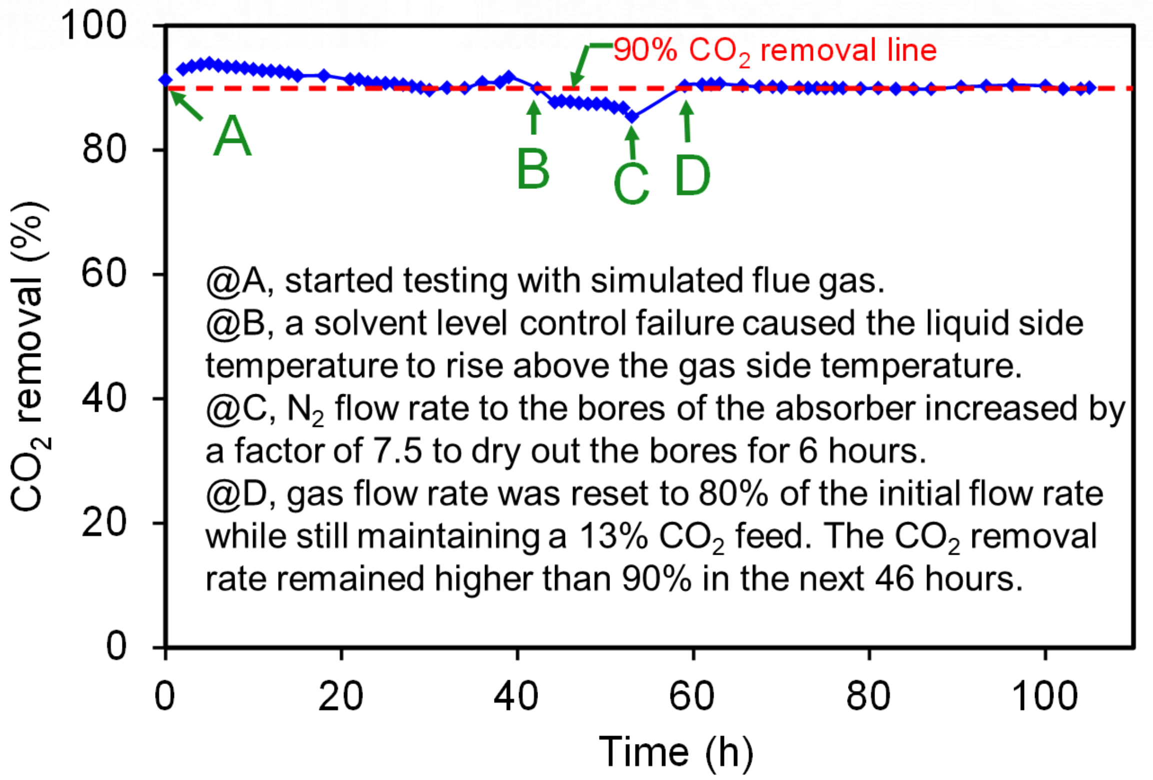
Membrane absorber

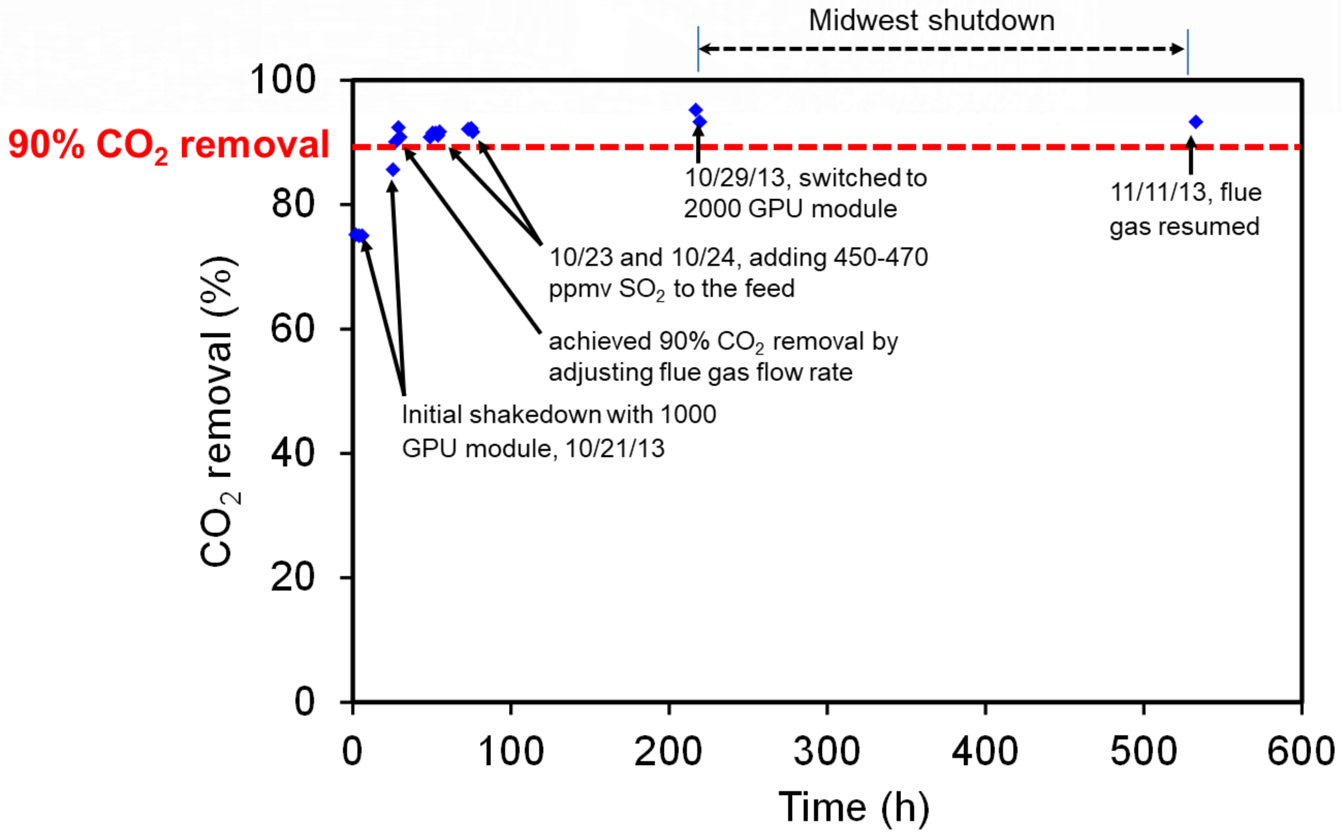
T (ºC)	P (psig)
40-60	1-20

Flash desorber

T (ºC)	P (psig)
~130	1-50

Integrated testing in the previous lab and bench (coal flue gas) project showed performance and stability





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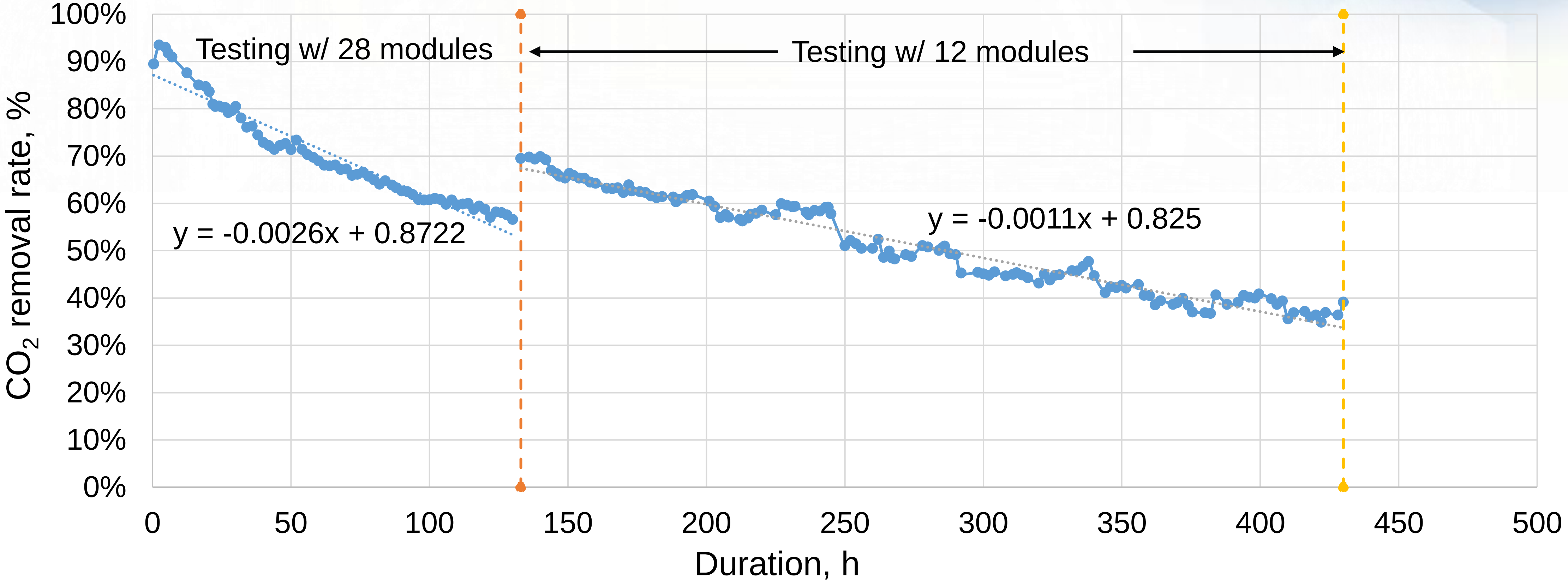
2018's testing with 28 membrane modules



- **Observation**: Performance declined with time
- **Analysis**: Quantitative analysis indicated three causes: 1) contaminants (powder and rust particles); 2) vapor condensation in fiber bores; and 3) capillary condensation of vapor in PEEK pores
- **Decision made at that point**: Resolve issue of contaminants (powder and rust particles) first

*Note: slope -0.0026 indicates a drop in 26% value per 100 hours

Additional flue gas filters and pre-membrane mesh pads installed to protect the membrane; orifice plates installed to monitor if there is a flow maldistribution issue

Installed new filters

Pre-membrane mesh pad

Liquid side Pressure gauge

Liquid side orifice plate

Gas side orifice plate

Gas side Pressure gauge

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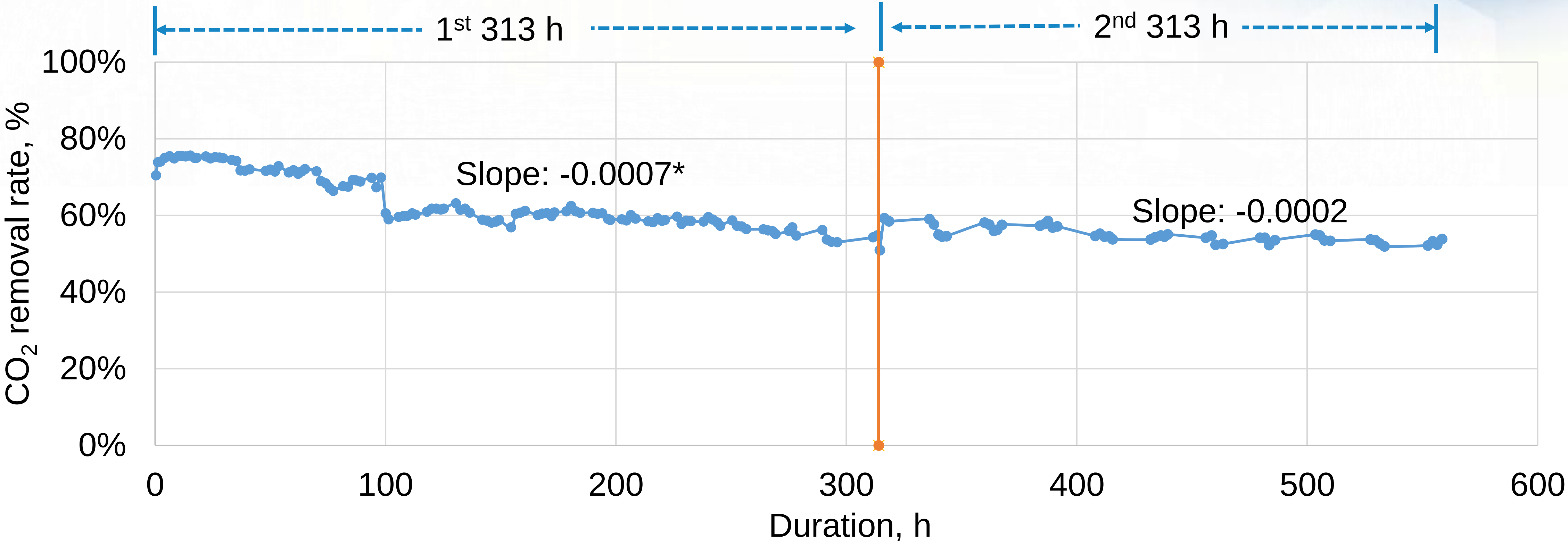
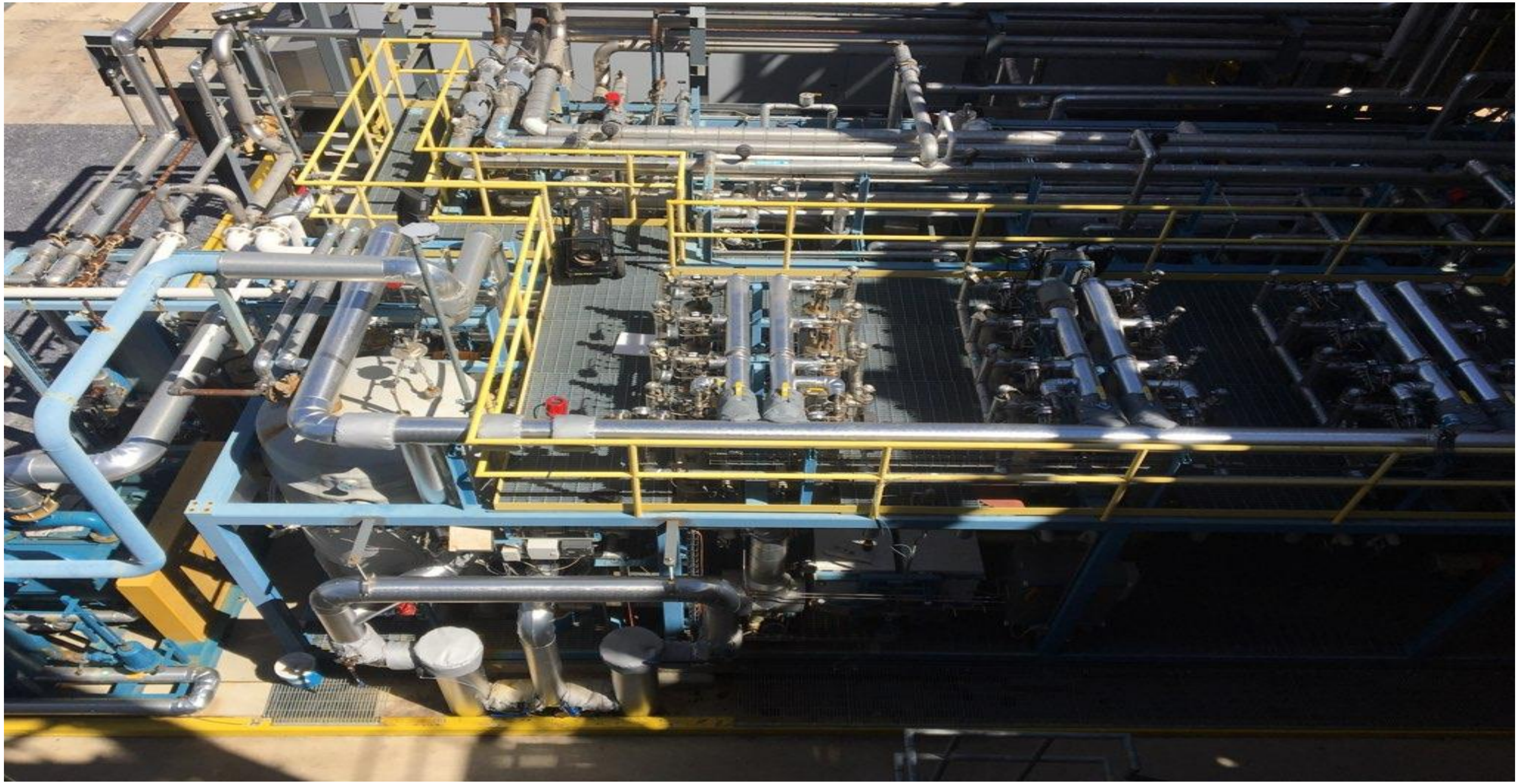
2019's testing with 8 modules (7 used and one new)



- **Observation**: stability improved, especially during the 2nd 313 h
- **Analysis**: 2% drop/100h during the 2nd 313h, might be because: 1) 7 used membranes (containing particles inside) were used, and 2) rusts from carbon steel piping; new membranes were expected to be stable
- **Decision made at that point**: move forward to fabricate 28 new membrane cartridges, replace carbon steel piping with stainless steel piping between filter and membrane header, and perform tests

*Note: slope -0.0002 indicates a drop in 2% value per 100 hours

Modified skid with stainless steel piping (February 2020)



2021's testing with 28 modules

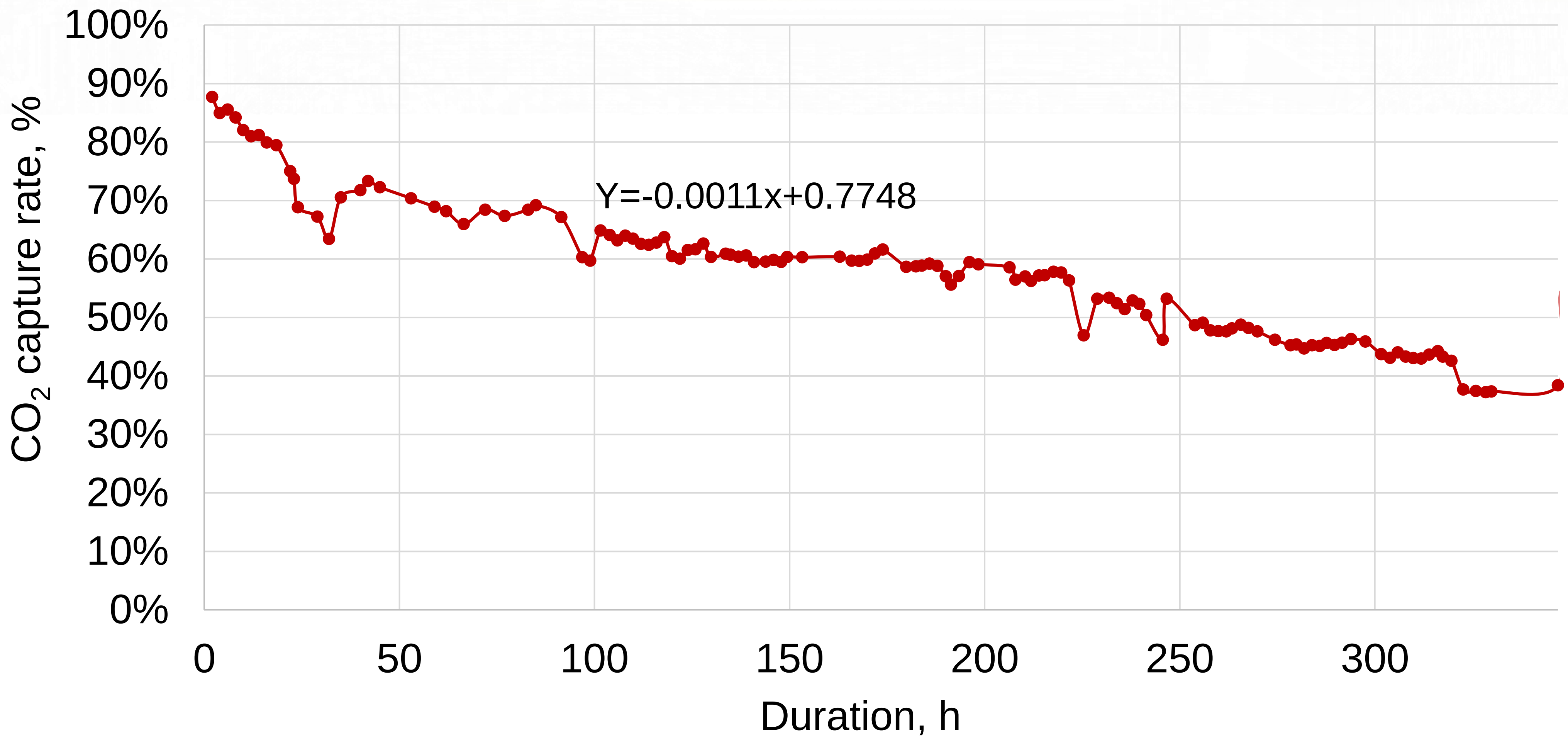
- **January 17**: Started testing
- **January 21** (system operated for ~92h): Shutdown due to power plant's shutdown
- **February 6:** Flue gas was back at NCCC, system brought back online
- **February 20** (system operated for ~347 total hours): Observed CO_2 capture rate dropped from 90% to ~39%. The decision was made to shut down system and look into approaches to recover performance and improve stability
- **February 20 – March 26**: Investigated: 1) approaches to recover performance, and 2) approaches to improve stability and performance
- **March 26**: System shutdown due to power plant's shutdown
- **March 26 – April 12**: Data analysis and reporting

Inspection: Inlet mesh pads were clean after system improvements, no visible rust or particulates present on the mesh pads, indicating the issue of particles had been resolved

Used mesh pad top surface after March 2019 testing: rust particles observed because between filter and membrane header carbon steel piping was used at that time

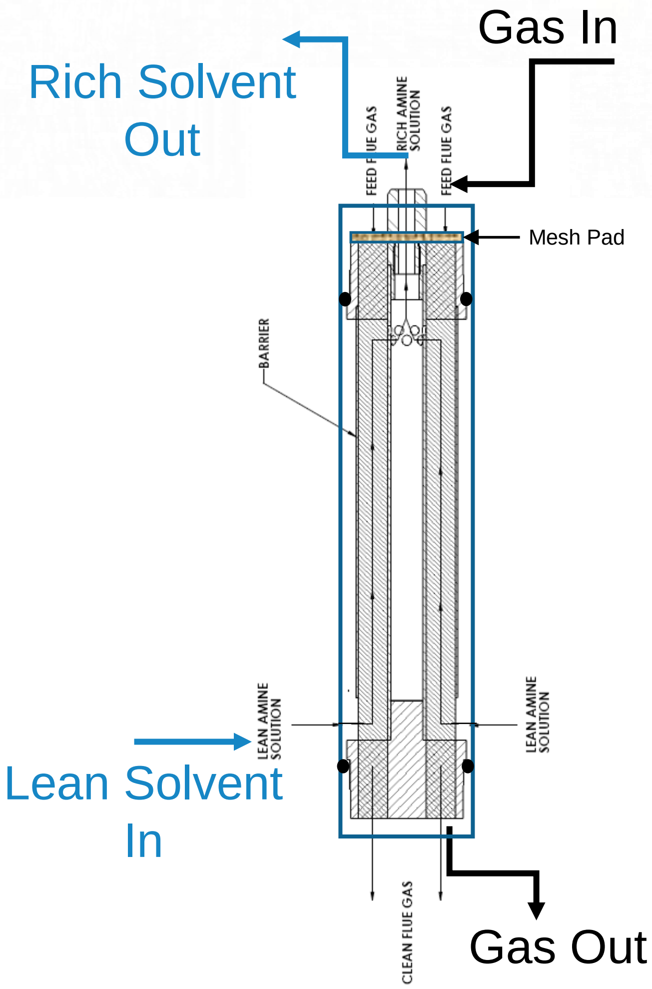
Used mesh pad top surface after 2021 testing: clean

2021's testing: Decline in performance observed for the 1st 347 hours with 28 modules



*Note: slope -0.0011 indicates a drop in 11% value per 100 hours

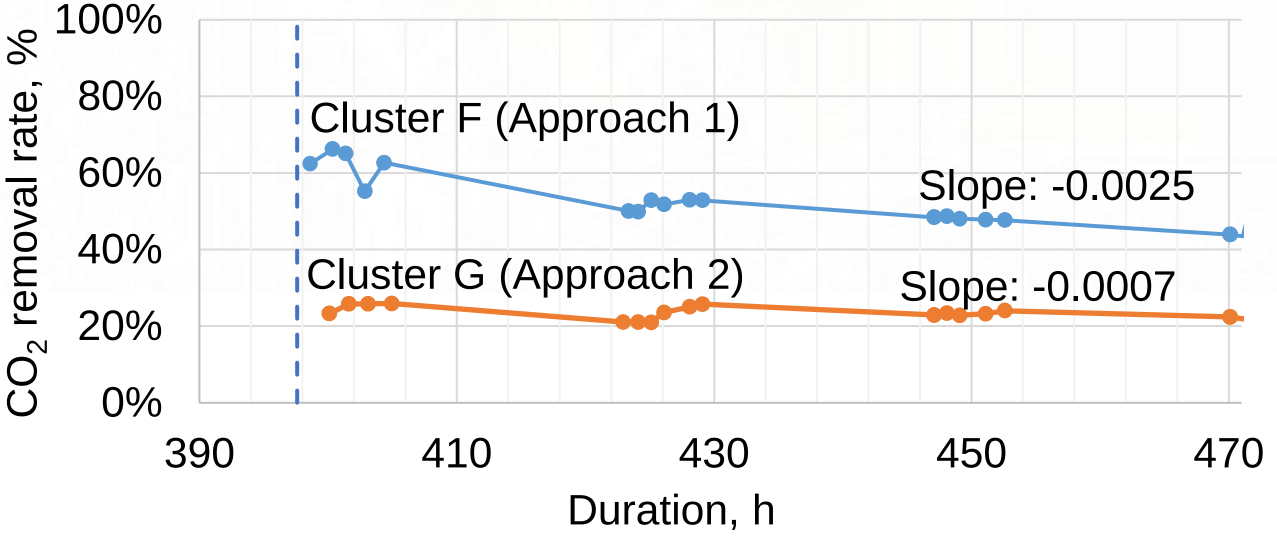
Approaches to recover membrane performance

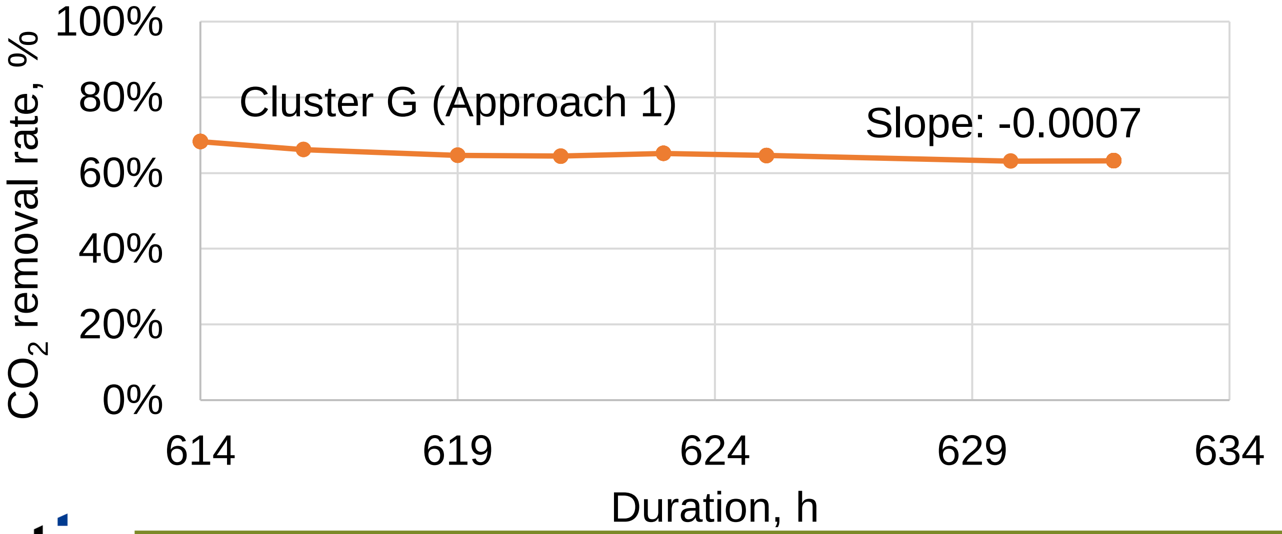


- **Approach 1**: Water wash followed by air dry
    1. Drain liquid from membrane shell side
    2. Remove inlet mesh pad
    3. Connect demineralized water to gas inlet, allow water to flow down to gas outlet
    4. Connect instrument air to the gas inlet, purge fibers with air
    5. Replace gas inlet mesh pad, bring membrane back online

- **Approach 2**: Air dry
    1. Drain liquid from membrane shell side
    2. Remove inlet mesh pad
    3. Connect instrument air to the gas inlet, purge fibers with air
    4. Replace gas inlet mesh pad, bring membrane back online

Performance can be recovered, but stability was not improved





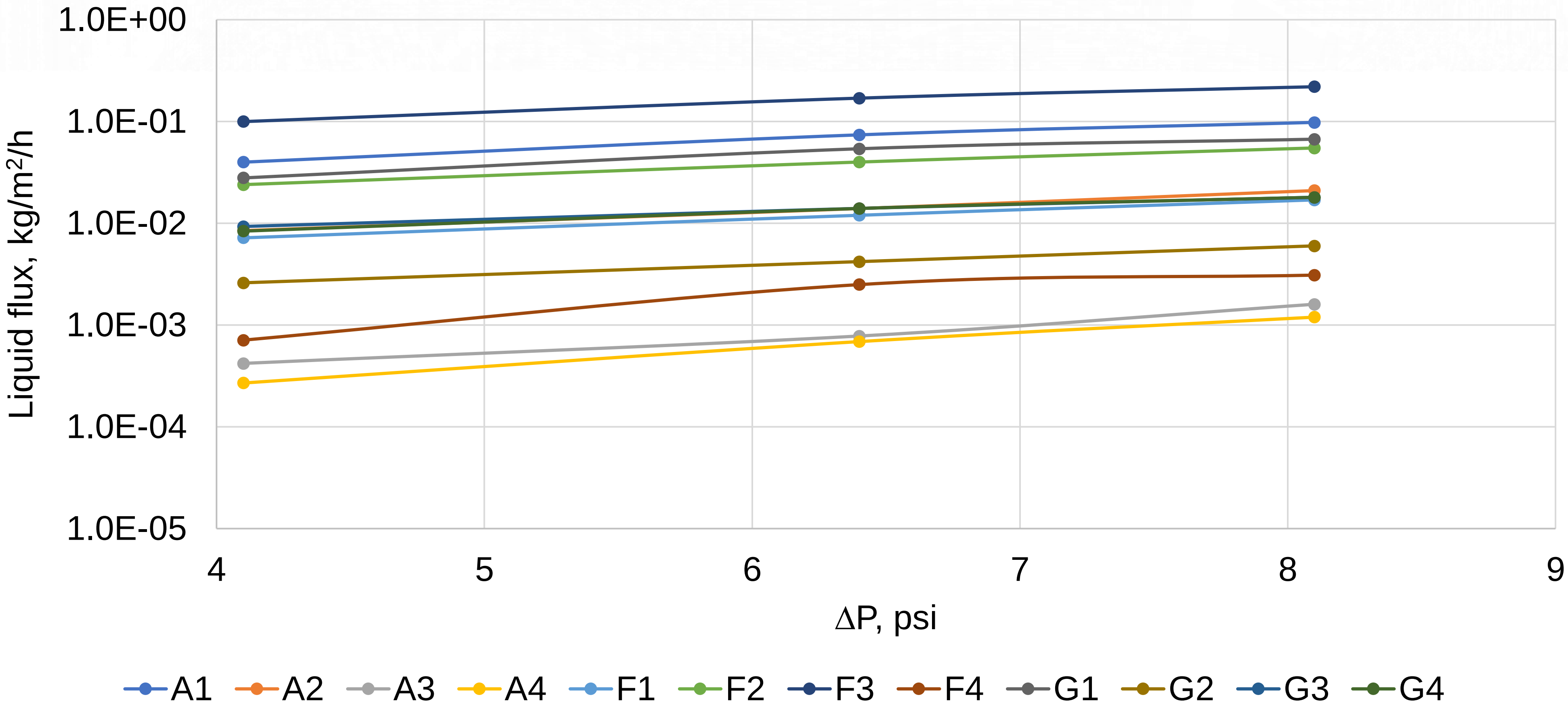
- Air purge alone was not sufficient in recovering performance
- Water wash + air purge can recover the performance but doesn't resolve continual decline issue

*Note: slope -0.0007 indicates a drop in 7% value per 100 hours

Performance degradation possible causes, actions and solutions

Cause #	Explanation	Sub-cause #	Explanation	Mitigating Information/Action Required to Resolve	Resolved?
1	Contaminants in the flue gas	A	Solids observed on inlet tubesheets and in bores	Replaced piping with stainless steel, installed filter, mesh pads in 2020	**Yes**
		B	Within bore or pore, water vapor condenses, blocking CO_2 passage	Reduced flue gas dewpoint with no effect on degradation. Liquid found in bore is consistent with amine, NOT flue gas	**Yes, verified not to be the cause**
2	Liquid was observed from the bore side drain with amine concentration close to solvent	A	Poor membrane potting into epoxy tubesheet provides a path	ALaS developed an infusion technique to eliminate leak path in 2016	**Yes, verified not to be the cause**
		B	Broken fibers during operations provide a path for amine to get into the top tubesheet and into the bores	Solvent permeation test, single gas permeation tests, and cyclohexane permeation tests on used modules	**Ongoing**
		C	Defects of the membrane superhydrophobic layer coating during handling or operation	SEM and other characterizations, Solvent permeation test, single gas permeation tests, and cyclohexane permeation tests on used modules	**Need action**
		D	Membrane hydrophobicity change (especially surface contact angle) after long-term contact with liquid	ALaS: measure contact angle as a function of time in the presence of solvent	**Need action**
		E	Vapor phase permeation of the solvent through the membrane and then condensation in the pores and in the bore	GTI: V-L-E data for amine solution, amine and water permeances to calculate the amine concentration of the condensed liquid; ALaS: prepare PEEK with pores > 50 nm (current pores have average size of 13-16 nm).	**Need action**

Testing underway to verify the causes of instability; solvent permeation tests suggest quality of the hydrophobic coating layer needs to be improved to be impermeable to solvent



Testing conditions: 65°F; shell side (solvent) pressure: 4.1, 6.4 and 8.1 psig; bore side pressure: ~0 psig

Summary

- Made modifications to skid – filters, stainless steel piping, mesh pads, 28 new membrane cartridges fabricated and installed
- Performed testing early 2021, solid issue resolved, decline in performance observed
- Developed an approach to recover performance, but stability was not improved
- Data analysis indicates most probable cause to instability: liquids in the pores
- Additional tests are ongoing to verify the causes of instability and resolve the issue

Acknowledgements

- **Financial and technical support**

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

Contract DE-FE0012829

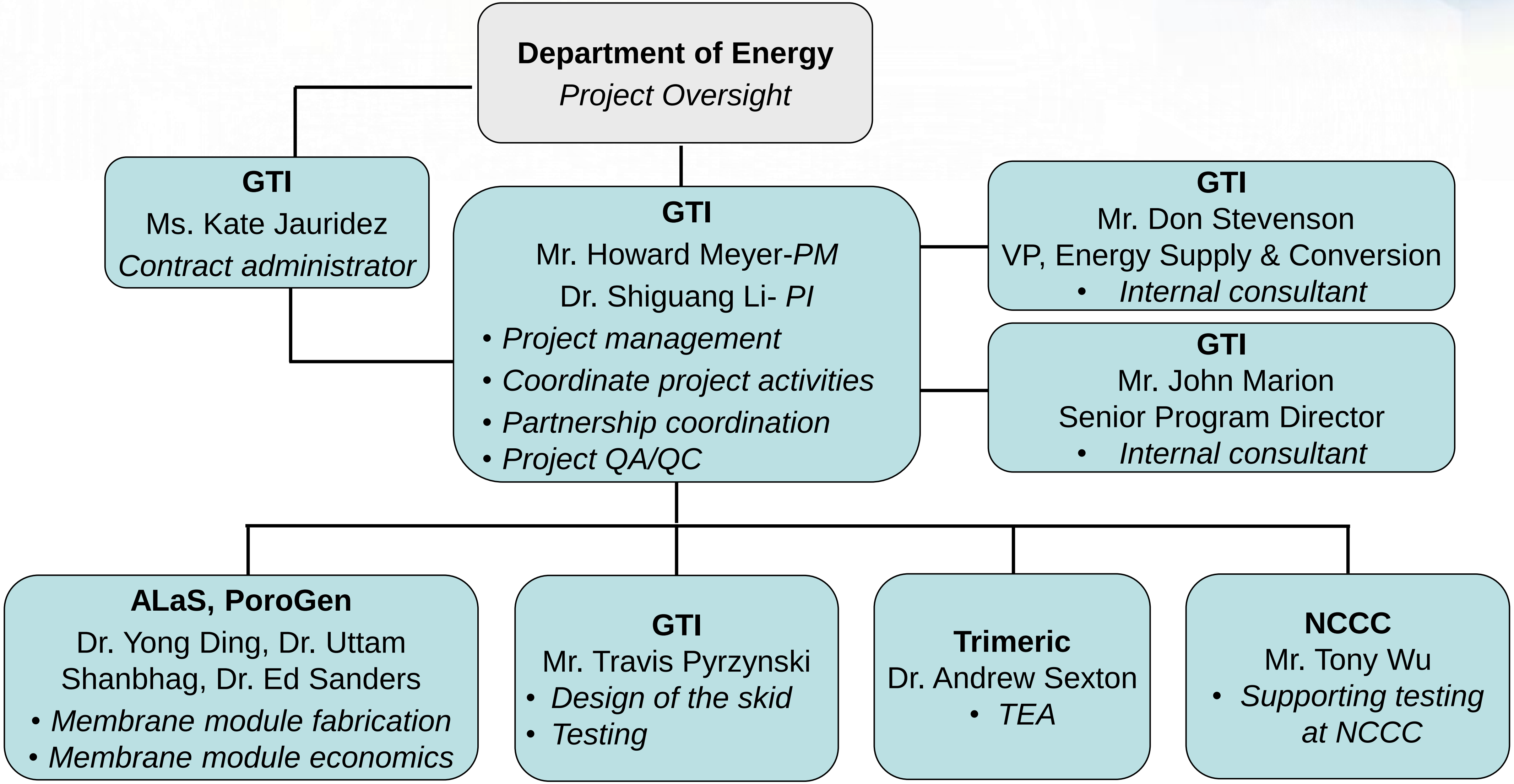
gti **JIP Partners**

Air Liquide ALaS

NATIONAL CARBON CAPTURE CENTER

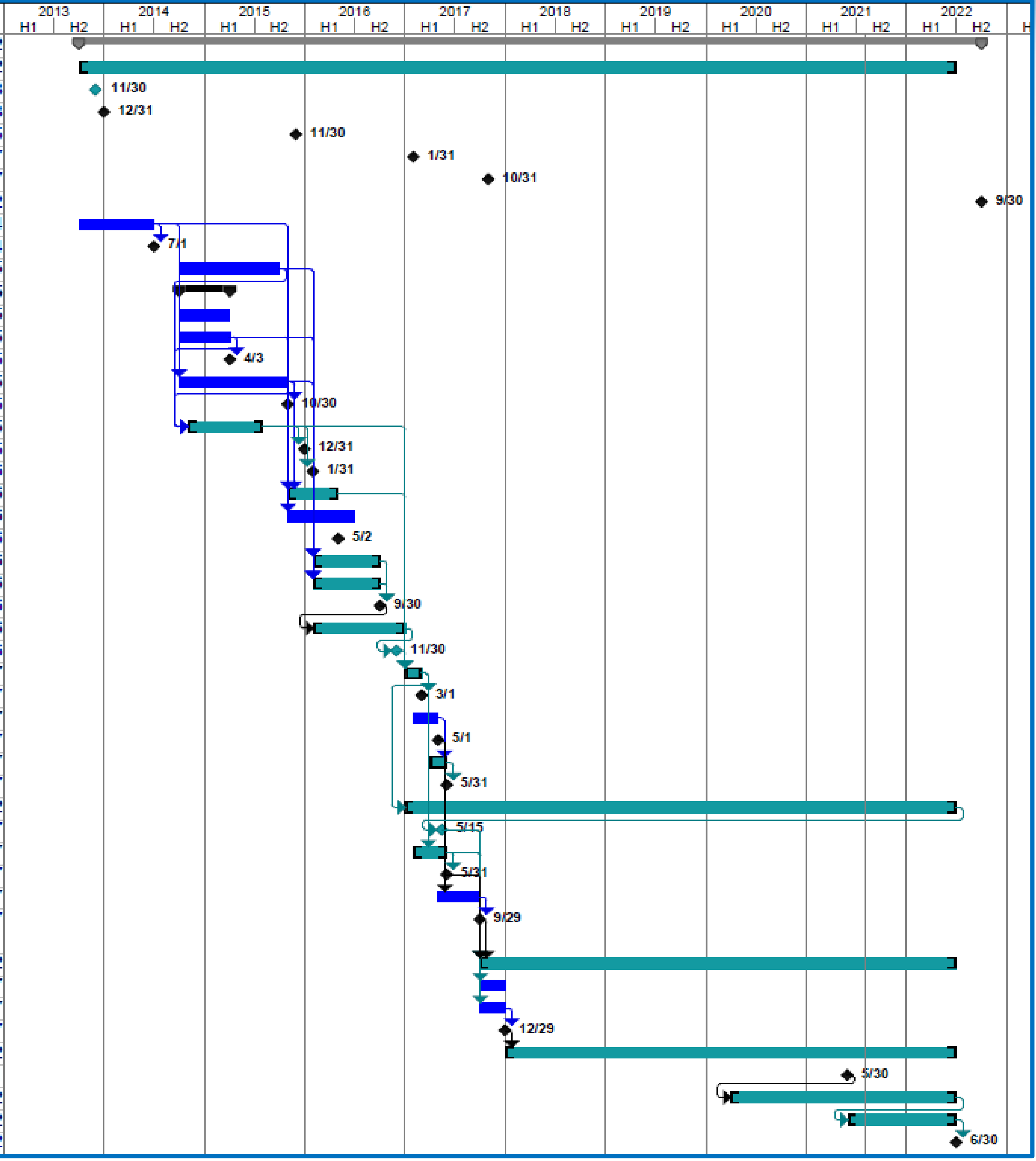
- **NETL: Andrew O'Palko, Steven Mascaro, Dan Hancu, José Figueroa, and Lynn Brickett**

Appendix – Organization Chart



Appendix – Gantt Chart

Task#	Task Name	Start	Finish
Project	**Budget and Schedule -September 2021**	**Tue 10/1/13**	**Fri 9/30/22**
Task 1.0	Project management and planning	Tue 10/1/13	Thu 6/30/22
M1.1	Updated Project Management Plan	Sat 11/30/13	Sat 11/30/13
M1.2	Kickoff Meeting	Tue 12/31/13	Tue 12/31/13
M1.3	Submit Budget Period 1 Report	Mon 11/30/15	Mon 11/30/15
M1.4	Submit Budget Period 2 Report	Tue 1/31/17	Tue 1/31/17
M1.5	Submit Budget Period 3 Report	Tue 10/31/17	Tue 10/31/17
M1.6	Submit Final Technical Report	Fri 9/30/22	Fri 9/30/22
Task 2.0	Preliminary techno-economic analysis and EH&S study	Tue 10/1/13	Mon 6/30/14
M2.1	Complete preliminary TEA and EH&S study	Tue 7/1/14	Tue 7/1/14
Task 3.0	Determination of scaling parameters for 2,000 GPU modules	Wed 10/1/14	Wed 9/30/15
Task 4.0	**Further testing in support of the pilot-scale design effort**	**Wed 10/1/14**	**Fri 4/3/15**
Subtask 4.1	QC testing of the PEEK hollow fiber membrane	Wed 10/1/14	Tue 3/31/15
Subtask 4.2	Membrane contactor testing and modeling	Thu 10/2/14	Fri 4/3/15
M3/4.3	Achieve CO2 permeances of 1,700-2,000 GPU in 2-inch modules	Fri 4/3/15	Fri 4/3/15
Task 5.0	Design of the 0.5 MWe equivalent CO2 capture system	Wed 10/1/14	Fri 10/30/15
M5.1	Issue pilot-plant design package	Fri 10/30/15	Fri 10/30/15
Task 6.0	Fabrication of 8-inch commercial-sized PEEK membrane modules	Sat 11/1/14	Fri 7/31/15
M6.1	Complete 8-inch diameter commercial size module fabrication	Thu 12/31/15	Thu 12/31/15
M6.2	Technical information about 8-inch diameter module delivered	Sun 1/31/16	Sun 1/31/16
Task 7.0	Determination of solvent conditions for CO2 capture using HFC	Sun 11/1/15	Sat 4/30/16
Task 8.0	Initial HFC CO2 capture performance testing for the 8-inch modules	Sun 11/1/15	Wed 6/29/16
M8.1	Achieve ≥90% CO2 removal	Mon 5/2/16	Mon 5/2/16
Task 9.0	Procurement of parts and subsystems for the 0.5 MWe system	Mon 2/1/16	Fri 9/30/16
Task 9.1	Fabrication of 8-Inch Modules for Pilot Plant Construction	Mon 2/1/16	Fri 9/30/16
M9.1	Complete procurement for the 0.5 MWe system	Fri 9/30/16	Fri 9/30/16
Task 10.0	Construction of the 0.5 MWe system	Tue 2/2/16	Sat 12/31/16
M10.1	Complete construction of the 0.5 MWe pilot system	Wed 11/30/16	Wed 11/30/16
Task 11.0	Site preparation	Sun 1/1/17	Wed 3/1/17
M11.1	Complete site preparation at NCCC	Wed 3/1/17	Wed 3/1/17
Task 12.0	System installation at the NCCC	Wed 2/1/17	Fri 4/28/17
M12.1	Complete pilot test system installation at NCCC	Mon 5/1/17	Mon 5/1/17
Task 13.0	On-site system shakedown	Sat 4/1/17	Wed 5/31/17
M13.1	Complete on-site system shake down at NCCC	Wed 5/31/17	Wed 5/31/17
Task 14.0	Fabrication of 8-inch diameter modules for pilot scale testing	Sun 1/1/17	Thu 6/30/22
M14.1	Sufficient 8" commercial size modules fabricated	Mon 5/15/17	Mon 5/15/17
Task 15.0	Procurement of solvents for pilot scale testing	Wed 2/1/17	Wed 5/31/17
M15.1	Sufficient solvents produced for pilot scale testing	Wed 5/31/17	Wed 5/31/17
Task 16.0	Parametric pilot-scale testing	Mon 5/1/17	Fri 9/29/17
M16.1	Achieve ≥90% CO2 removal under realistic flue gas feed conditions in one stage, membrane module CO2 capture flux ≥0.32 Kg/m2/h	Fri 9/29/17	Fri 9/29/17
Task 17.0	Module modification based on pilot-scale testing results	Sun 10/1/17	Thu 6/30/22
Task 18.0	Solvent process adjustment based on pilot-scale testing results	Mon 10/2/17	Fri 12/29/17
Task 19.0	Identification of continuous steady-state operation conditions	Mon 10/2/17	Fri 12/29/17
M19.1	Conditions for continuous steady-state operation identified	Fri 12/29/17	Fri 12/29/17
Task 20.0	Continual steady-state operation	Mon 1/1/18	Thu 6/30/22
M20.1	Complete a continuous operation for a minimum of two months	Sun 5/30/21	Sun 5/30/21
Task 21.0	Engineering support	Wed 4/1/20	Thu 6/30/22
Task 22.0	Removal of pilot system	Tue 6/1/21	Thu 6/30/22
M22.1	Pilot scale system removed, site cleaned up	Thu 6/30/22	Thu 6/30/22



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