Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes

Phase I Final Review

Contract No.: DE-SC0017124
SBIR Topic: 17C
Period of Performance: 2/21/17 – 11/20/17
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Contractor: Luna Innovations Incorporated

LUNA

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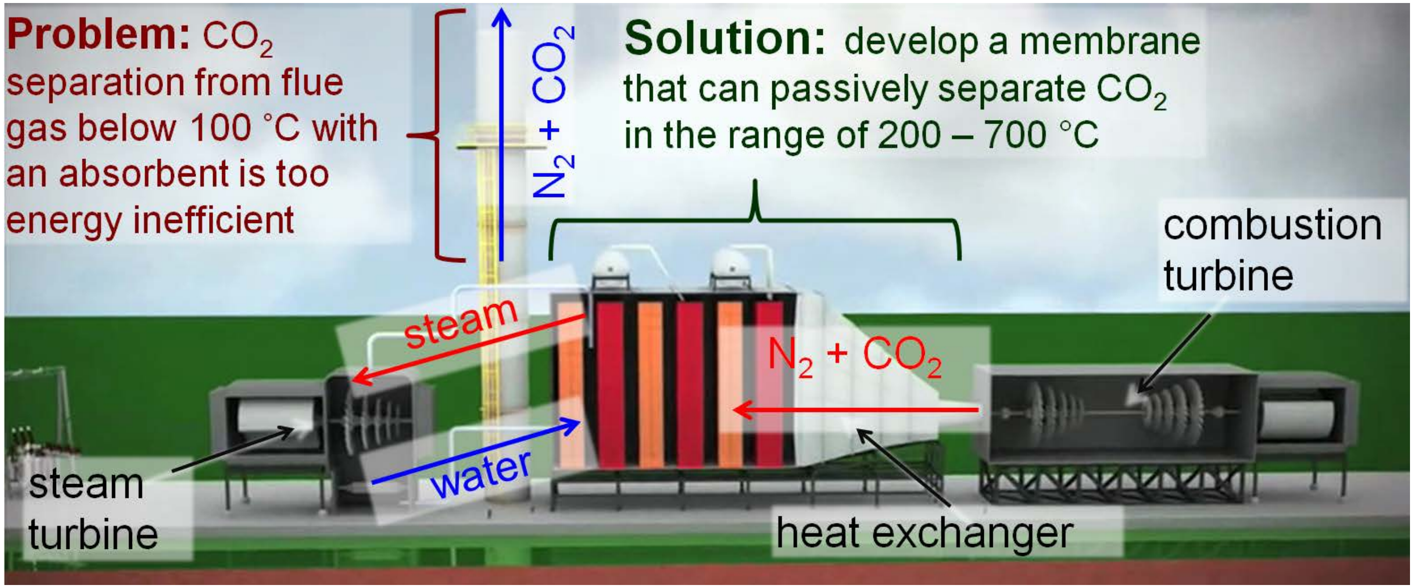
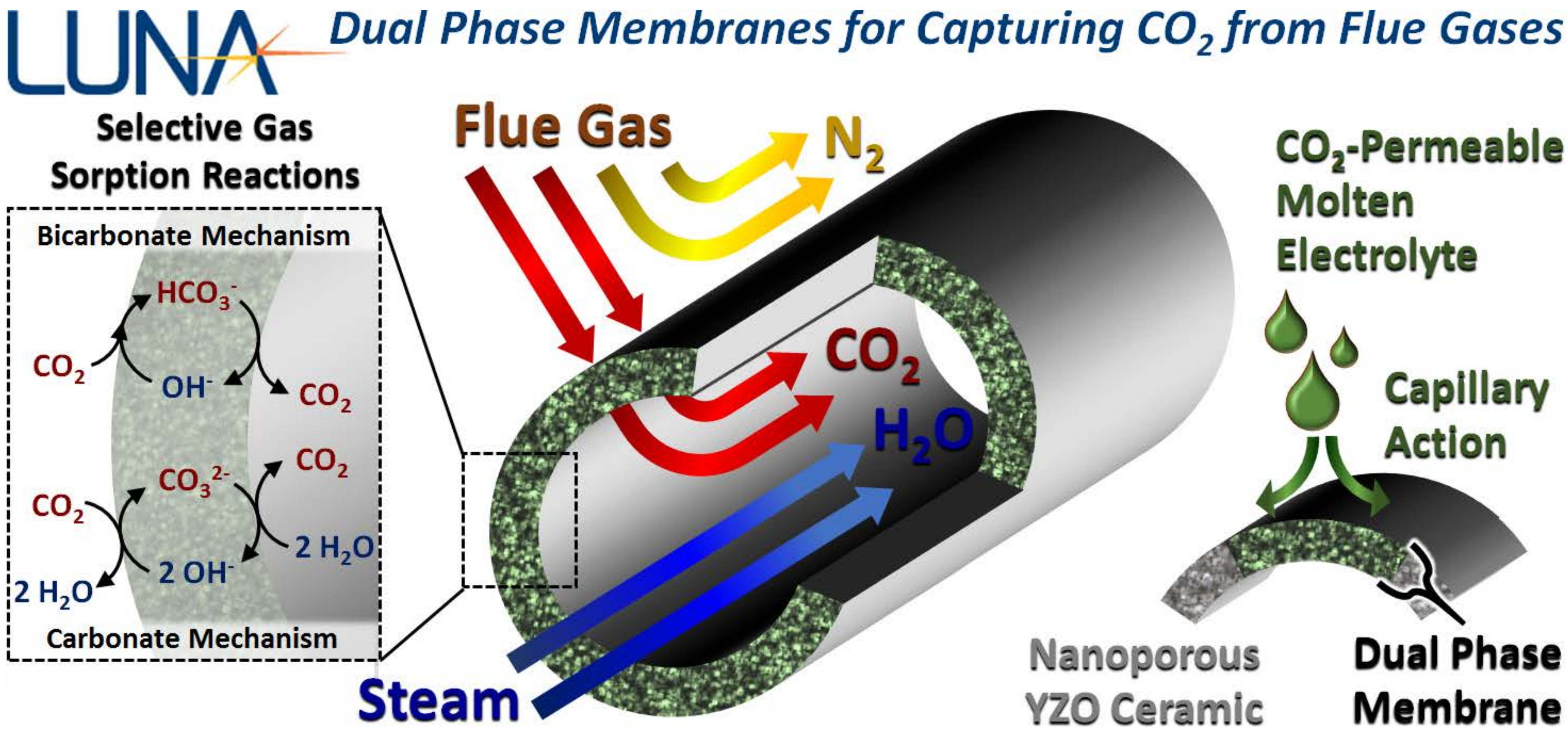
November 30, 2017

Problems and Solutions



- A cost effective technology is needed for carbon capture
  - Incremental improvements in conventional technologies are insufficient
- Energy: avoid Carnot inefficiency of additional heat cycles and gas compressions
  - Establish passive membrane separation of CO_2 from flue gas
- Infrastructure: simple, effective integration with existing technology
  - Incorporate modular membrane technology into modular hear recovery steam generators (HRSG)

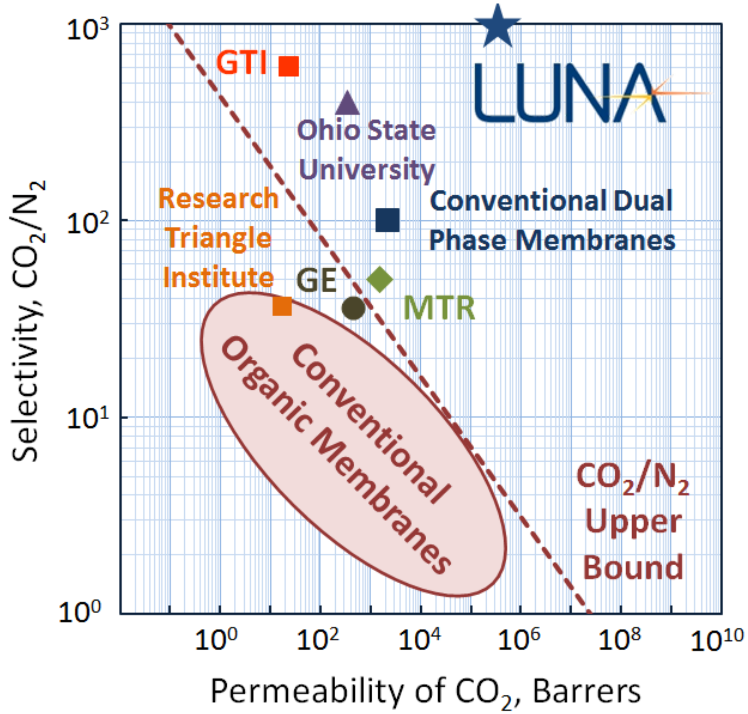
Dual Phase Membranes



- Critical innovations: reformulate electrolyte and apply steam sweep
  - All mass transport in liquid phase for faster separations and lower operational temperatures
  - Original inventers: Electrolyte - Merrill (Luna), Ceramic – Campbell (LLNL), Membranes – Kim (UIC)

LUNA | Performance and Capability

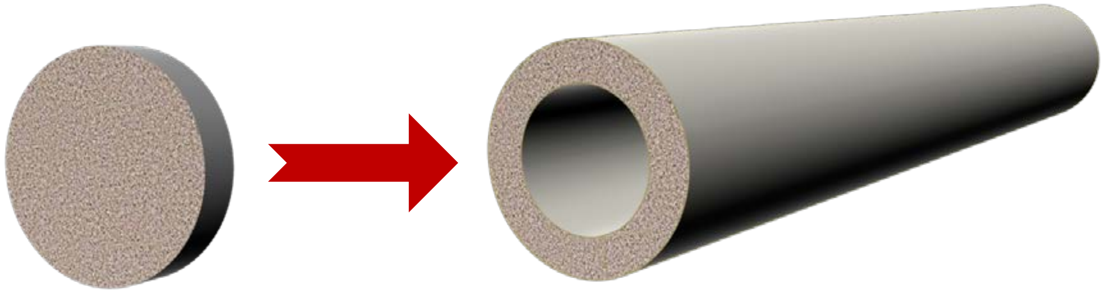
- Technology more similar to a fuel cell or battery than conventional membranes
  - $H_2O_{(g)}$ pressure gradient enables capture from unpressurized flues gas even at low CO_2 concentrations
- Unrivaled combination of selectivity and permeability
  - Not limited by physics governing Robeson's Upper Bound
- Stable inorganic materials enable operation in previously unattainable conditions
  - Temperatures: 200 – 700 °C
  - Pressures: 0.1 – 30 ATM
  - Oxidative or corrosive environments
- Separation chemistry adaptable to NH_3, HCl, O_2, Cl_2, and NO_2 for widespread applications



- Ohio State University, 2017 NETL Continuation Application Status Meeting
- Membrane Technology and Research (MTR), NETL Advanced CO_2 Capture R&D Program Technology Update May 2013
- Research Triangle Institute, 2013 NETL Advanced CO_2 Capture R&D Program Technology Update
- General Electric (GE), 2013 NETL Advanced CO_2 Capture R&D Program Technology Update
- Gas Technology Institute (GTI), 2017 NETL BP1 Review Meeting
- Lu, B. and Lin, Y.S., Journal of Membrane Science 444 (2013) 402–411

LUNA | Phase I Program Scope

Lab Scale Discs



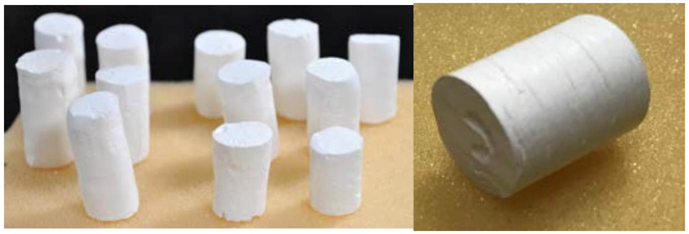
Manufactured Tubes

- Phase I Scope: Scale up technology for tube membrane capabilities
- Objective 1: Prepare solid phase materials
  - Scale up production capabilities from discs to cylinders, square bar, and tubes
- Objective 2: Characterize thermo-mechanical and chemical stability
  - Characterize mechanical properties and fatigue under accelerated conditions
  - Optimize properties of solid phase/molten electrolyte interface
- Objective 3: Develop design tools and test a designed tube
  - Develop modeling and design tools
    - MatLab analysis, computer assisted design (CAD) and finite element modeling (FEM)
  - Produce and test a tubular design

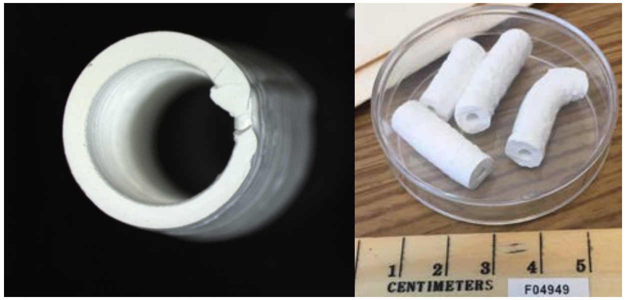
Task 1: Porous Solid Phase Material Production

- LLNL to produce porous yttria-doped zirconium oxide (YZO) test materials
  - Discs for membrane testing
  - Cylinders for compression testing
  - Square bar for flexural/tensile strength testing
  - Tubes for advanced membrane design testing
- Good material performance properties
  - Density, electrolyte uptake, pore hierarchy
- Manufacturing capabilities need improvement
  - Defects and non-uniformity concentrate stress, lower effective strength, limit membrane performance
- ***Risk: timely receipt of suitable tubes***
  - Obtain critical test materials from alternate source

1^{st} (inset) and 4^{th} square bar batches upon arrival



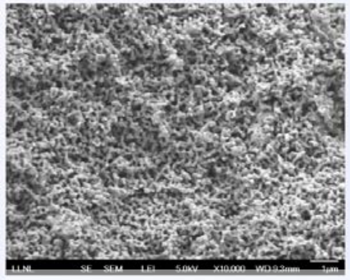
1^{st} (left) and 3^{rd} (right) cylinder batches



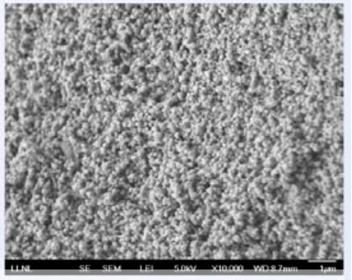
3D printed Extruded

LUNA | Task 1: Porous Solid Phase Material Production

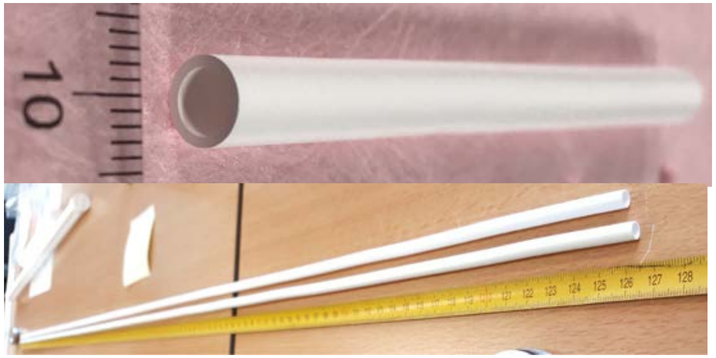
- CoorsTek porous YZO materials
  - Injection molding (discs) and extrusion (tubes)
    - First time extruding porous YZO
  - Off-the-shelf formulation, mold, and die
  - 100 nm pore size (Same as LLNL's YZO)
  - 1.5 times more dense than LLNL's YZO
    - Higher density slows separation rates
  - Uniform, consistent dimension
- Discs for surface catalytic/wetting effects
  - 70 mm diameter and 2.2 mm thick
- Tubes for scaling up membranes
  - 6.35 mm OD, 4.78 mm ID, 10 cm long
  - With and without fully dense end caps
  - Produce tubes up to 1.2 m in length



LLNL: 35.9 wt% molten phase uptake



CoorsTek: 17.5 wt% molten phase uptake



CoorsTek tubes

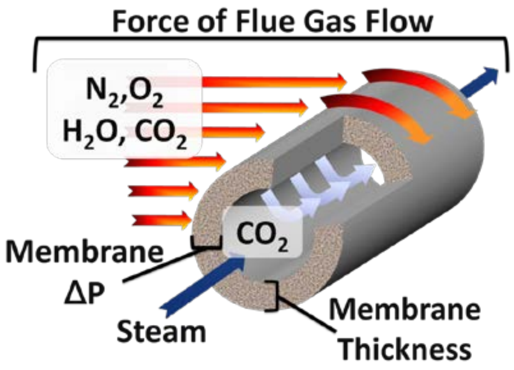
Task 2: Characterize thermo-mechanical properties

- Need to understand membrane mechanical properties to develop design
  - Minimize membrane thickness to maximize separation rates
  - Design the withstand stresses and forces of operational conditions
  - Scale dimensions to improve packing efficiency for smaller footprint in HRSG
- Mechanical strength testing of LLNL and CoorsTek materials
  - Square bar samples per ASTM C1161: flexural and tensile strength
  - Right cylinder samples per ASTM C773: compressive strength
- CoorsTek materials about 5 – 10 times stronger than LLNL materials
  - CoorsTek materials can enable much faster separation rates with thinner membranes

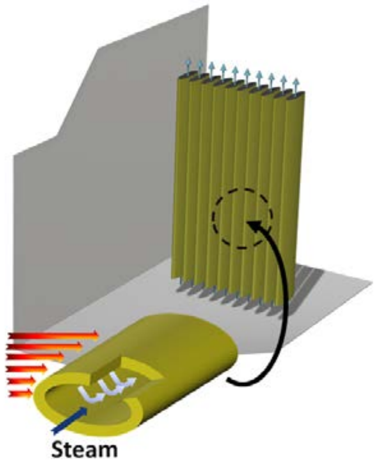
Material	Relative Density (%)	Porosity (%)	Compressive Strength (MPa)	Flexural Strength (MPa)	Tensile Strength (MPa)
Fully Dense YZO (CoorsTek)	100	0	2000-2500	900 - 1250	700-900
Macroporous YZO (Literature)	50 - 60	40 - 50	60 - 80	25 - 35	15 - 25
Nanporous YZO (LLNL)	40	60	5.9	6.7	4.7
Nanoporous YZO (CoorsTek)	55	45	15 - 25	24	16

LUNA | Task 4: Tube Level Analysis

- Develop design tools for circular and elliptical tubing
  - MatLab stress analysis for initial tube dimensional requirements
  - NEiNastran Finite Element Analysis (FEA) to model simulated loads, fatigue, and failure
  - Solidworks CAD models to improve performance and integration
- Design considerations
  - Nooter/Eriksen: steam inside of tube and flue gas outside of tube
    - N/E's "Low Pressure" steam at 4.2 ATM has a higher pressure than the flue gas at ~1 – 1.2 ATM
  - Smaller tube diameters enable thinner walls at a given pressure
    - Thinner walls enable faster separation rates
  - Smaller tube diameters enable more total membrane surface area per m^3 of HRSG space
  - Smaller tube diameters have slower gas flow rates inside tube



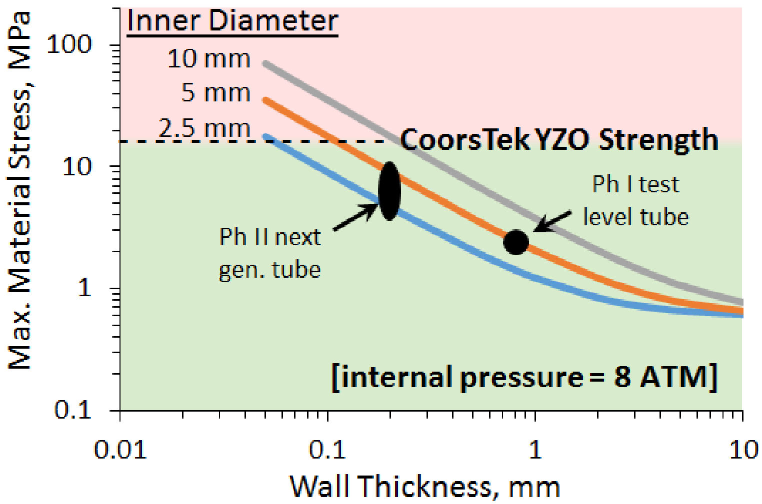
Demonstrate circular tube membrane in Phase I



Design elliptical tube for Phase II assembly of HRSG membrane module

Task 4: Test Level Circular Tube

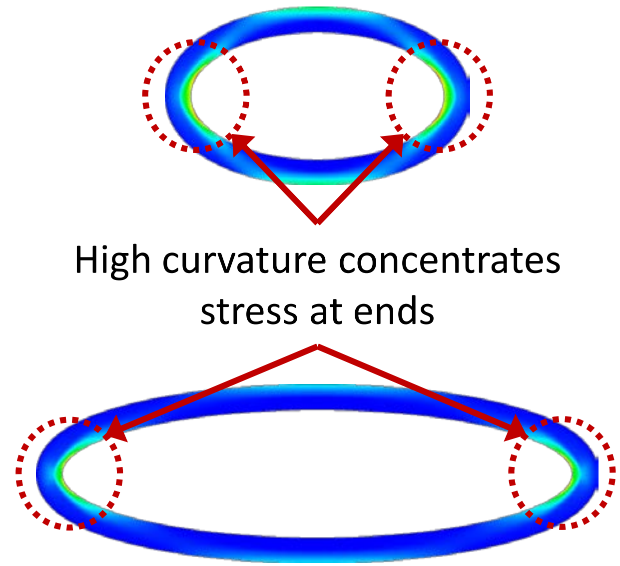
- Modeled maximum material stress as a function of pressure and tube dimensions
  - Tubes better withstand external pressure
    - Limited by the larger compressive strengths
  - N/E wants the higher steam pressure inside tube
    - Limited by the weaker tensile strength
- Phase I CoorsTek YZO tubes
  - 6.35 mm OD, 4.78 mm ID, 0.79 mm wall thickness
  - CoorsTek tubes extruded to 1.2 m length
  - Test samples cut to 10 cm
- Phase II scale down in tube size
  - CoorsTek has extruded 0.2 mm thick walls in other applications: 4X decrease
  - Budget cost of making a new extrusion die



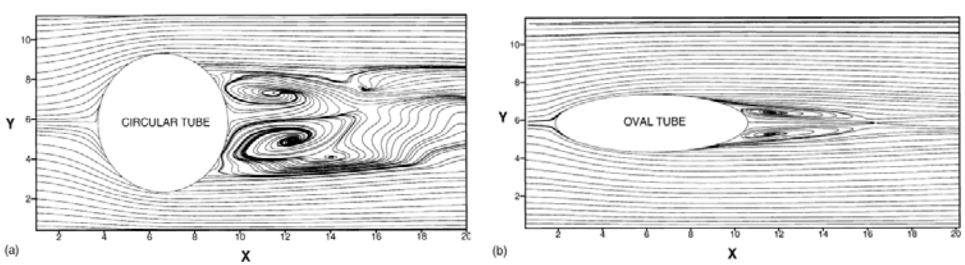
CoorsTek materials are strong enough to scale to thinner walls even when internal pressure is 2X greater than expected!

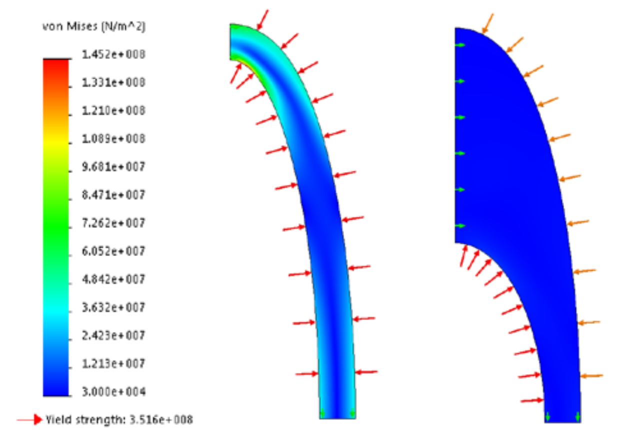
Task 4: Elliptical Tube Design

- Elliptical tubes advantageous for HRSGs
  - Ellipses increase contact time and lower pressure drops for flue gas flowing over tube
  - Ellipses increase membrane surface area per volume
  - Volumetric packing efficiency increase by 3 – 5X
- Ellipses analyzed with 2X and 4X aspect ratios
  - Too much stress concentrates with uniform wall thickness
  - Increased wall thickness at ends removes stress concentration

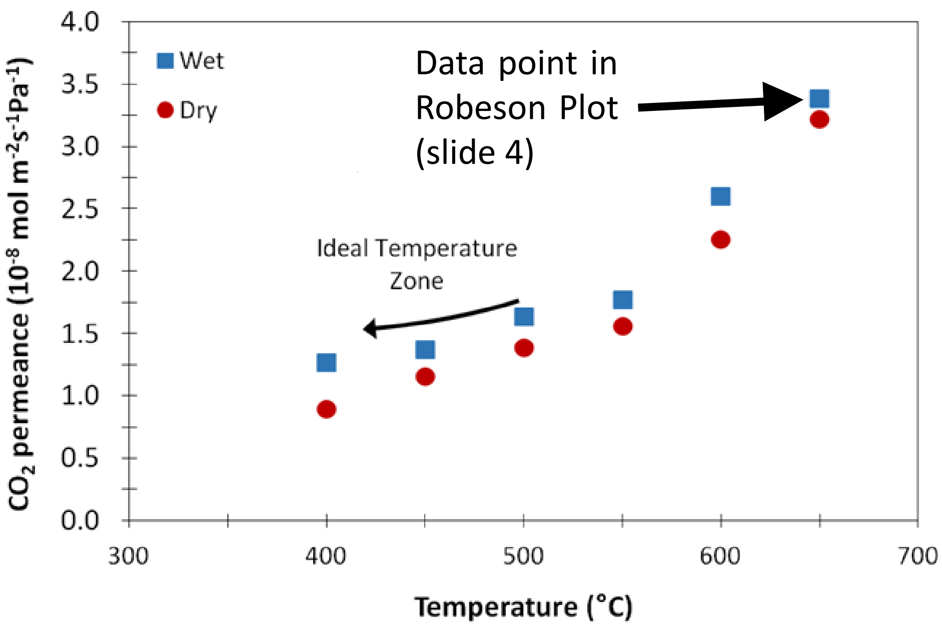


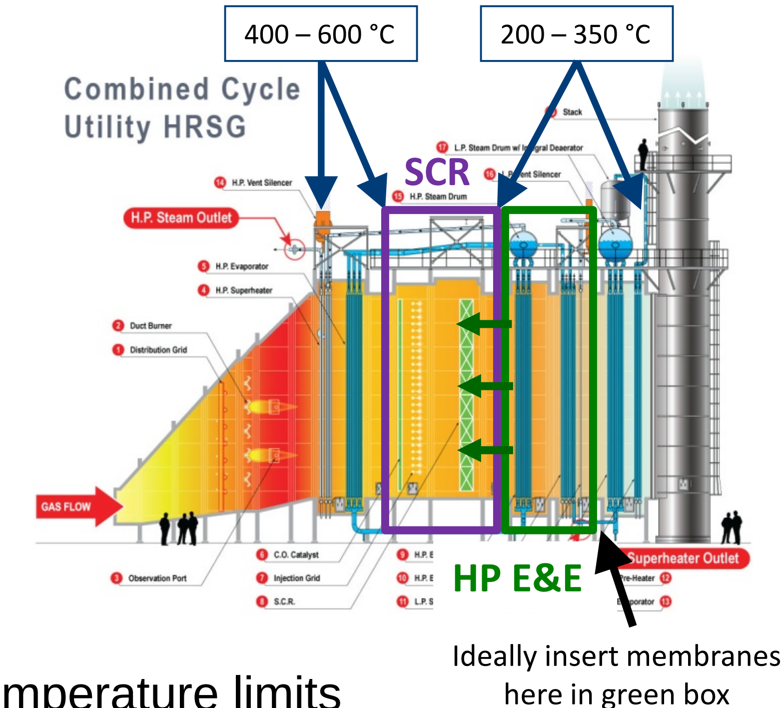
Elliptical shape increases contact time and lowers pressure drop for flue gas flowing over outside of tube membrane





Task 4: HRSG Integration





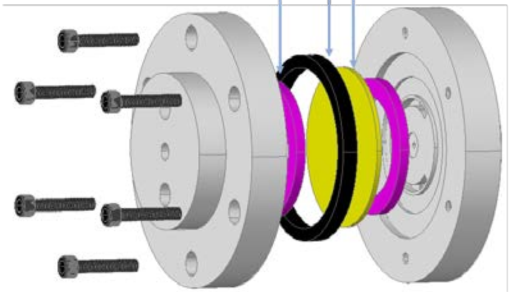
- Experimental membrane testing for low temperature limits
  - Ideally, membrane modules would operate in the 300 – 400 °C for HRSG integration
  - The low temperature limit presently limited by electrolyte composition and water vapor pressure
    - Phase II will include developing test setup to increase $H_2O_{(g)}$ from 0.08 ATM to 1 – 6 ATM
    - Phase II program will also include modifying the electrolyte for lower temperatures
- Phase II tubes will enable packing membranes in 3 – 4 m of HRSG length

Task 5: Testing CoorsTek Discs

- CoorsTek injection molded 70 × 2.2 mm discs
  - Used a previously developed disc mold
  - 70 mm discs to large for UIC's initial setup
  - Testing 25 mm discs cut from 70 mm discs unsuccessful
  - UIC fabricated a membrane holder for 70 mm discs
- Achieving leak-free testing of 70 mm discs unsuccessful
  - Graphite gaskets can pass initial leak tests at room temperature but leak at operational temperatures
  - Leak-free membranes have selectivity > 1,000 CO_2 per N_2/Ar
    - Below gas chromatograph detection limit
- CoorsTek materials achieve high performance
  - Disc fragment successfully tested with mounting method
  - The difference in LLNL and CoorsTek permeability correlates with effective porosity

Leak-free performance at 20% CO_2 and 550 °

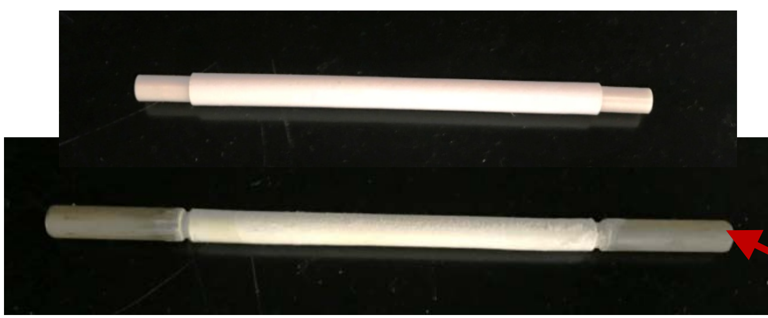
	Coorstek	LLNL
CO_2 permeability (Barrer)	1.9×10^5	2.4×10^5
Selectivity CO_2/Ar	> 1,000	> 1,000
Effective porosity, %	25	43



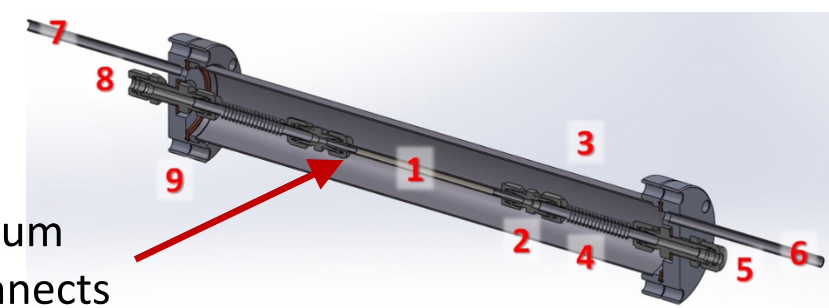
Membrane holder for 70 mm discs

LUNA | Task 5: Testing CoorsTek Tubes

- Luna designed and built the tube membrane holder
  - The solid YZO end caps of the sample (**1**) sealed with ceramic adhesive to titanium interconnects (**2**) to match thermal expansion
  - Flexible tubing (**4**) relieves stress during assemble and operation
  - Sample holder sits inside split tube furnace
- Successfully loaded samples leak-free at room temperature but leak at operational temperature
  - Selectivity indicates it's a leak at an interconnect/interface and not pinhole in the sample
- UIC has remaining materials and will continue testing



Titanium interconnects



Conclusions

- Successfully developed the material readiness level of the solid phase YZO
  - CoorsTek materials can support the Phase II development of membrane modules
    - Separation membrane performance of CoorsTek materials as good as LLNL materials
    - Commercial injection molding and extrusion manufacturing capabilities
    - Expertise in customized form factors, tooling, and design guidance
- Nanoporous YZO materials strong enough to support performance and dimensional requirements for HRSG integration
  - Scale down to thinner membranes while enabling targeted steam pressure requirements
  - Obtain surface area packing efficiency requirements with minimal flue gas pressure drop
- Unique separation capabilities
  - Superior combination of permeability and selectivity
  - Enable separation at temperatures as low as 400 °C to date

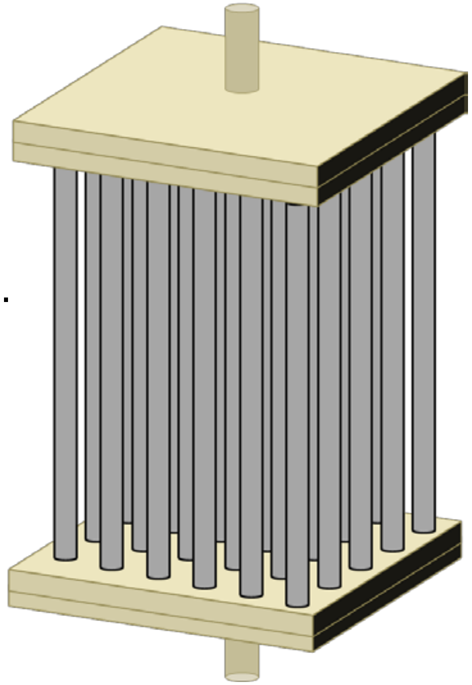
LUNA | Phase II Objectives

Overall Goal

- Design, develop, and manufacture a separation module for pilot-scale testing at the National Carbon Capture Center (NC3).

Phase II Objectives

- **Objective 1:** Scale up from single tubes to membrane modules
  - Concept module (5 short tubes): Develop and validate design features (i.e. interconnects) and manufacturing processes
  - Prototype module (~30 long tubes): Demonstrate and characterize separation performance
- **Objective 2:** Evolve testing and performance capabilities: apply steam, evaluate NO_X effects, modify electrolyte for lower temperatures, test prototype module at NC3.
- **Objective 3:** Develop and model integration with HRSGs: infrastructure requirements, system level analysis.



LUNA | Phase II Team

- Nooter/Eriksen
  - Perform CFD modeling, HRSG integration, system level analysis
  - Expressed interest in manufacturing and selling the CO_2 separation technology
- UIC
  - Single tube testing: stability, NO_X, low temp. electrolyte
  - Develop module testing at Luna: Engineers need hands-on experience for failure analysis
- LLNL
  - Nominal development of YZO 3D printing capabilities
- CoorsTek (materials supply only)
  - Produce Ph I test level tubes, Ph II thinner tubes, module flange

LUNA | Questions?

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- 3. Wade, J.L., et al., Composite electrolyte membranes for high temperature CO_2 separation. Journal of Membrane Science, 2011. 369(1): p. 20-29.
- 4. Xing, W., et al., Steam-promoted CO_2 flux in dual-phase CO_2 separation membranes. Journal of Membrane Science, 2015. 482: p. 115-119.