STTR – DE-SC0005004
Advanced Technology for He Recovery

Helios-NRG, LLC

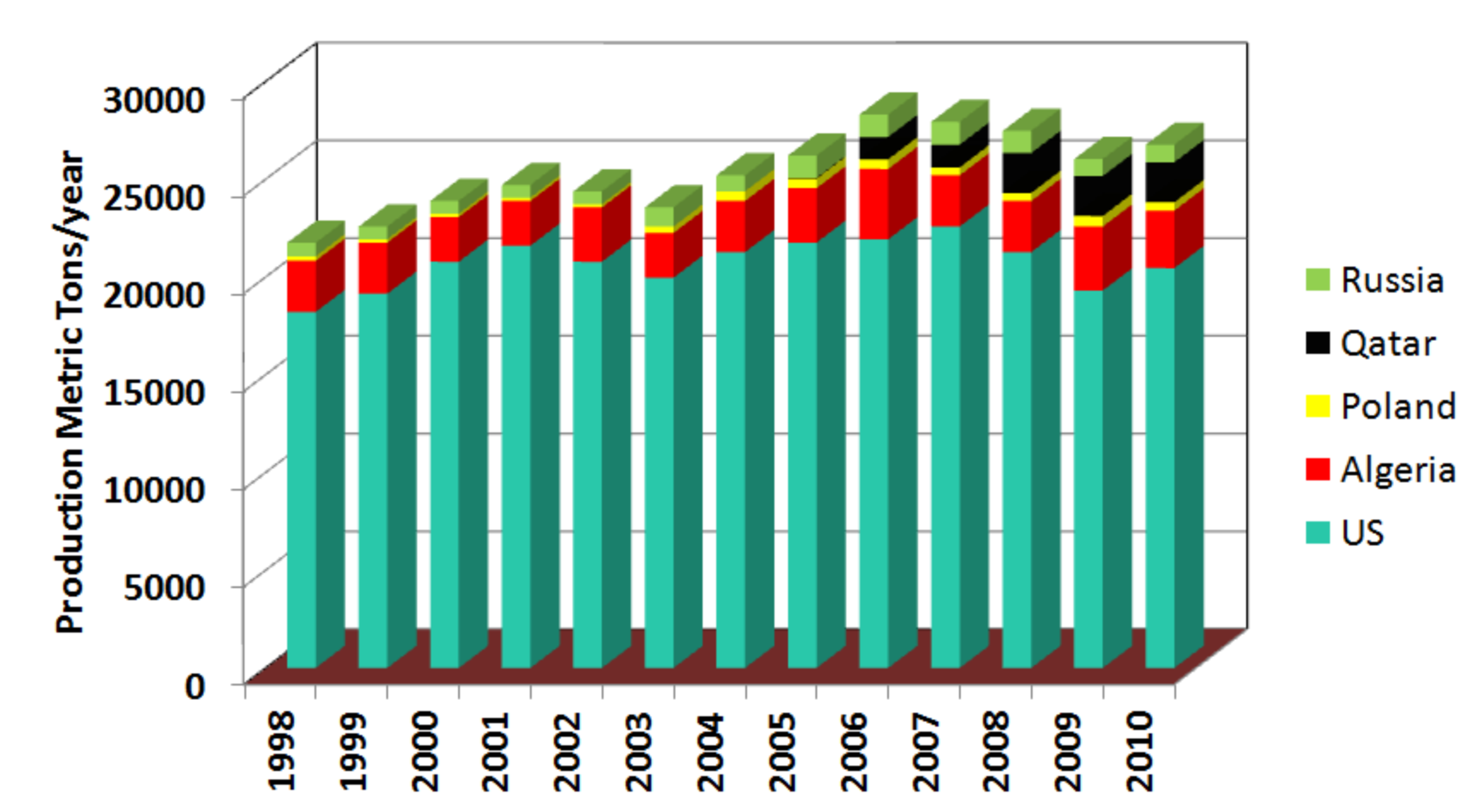
OAK RIDGE National Laboratory

MTR Membrane Technology & Research

He Overview

- **He has unique properties**
  - 2nd lightest; Smallest molecule
  - Most Inert; Highest ionization potential
  - Lowest boiling point (~4K)
  - Excellent heat transfer
- **Helium is a strategic resource**
  - Scarce - economically recoverable from only a few natural gas deposits around the world (~>0.3% He typically required)
  - The quantity of He on earth is in constant decline
  - Used in a large number of critical applications where use of an alternative is difficult/impossible

Global He Production



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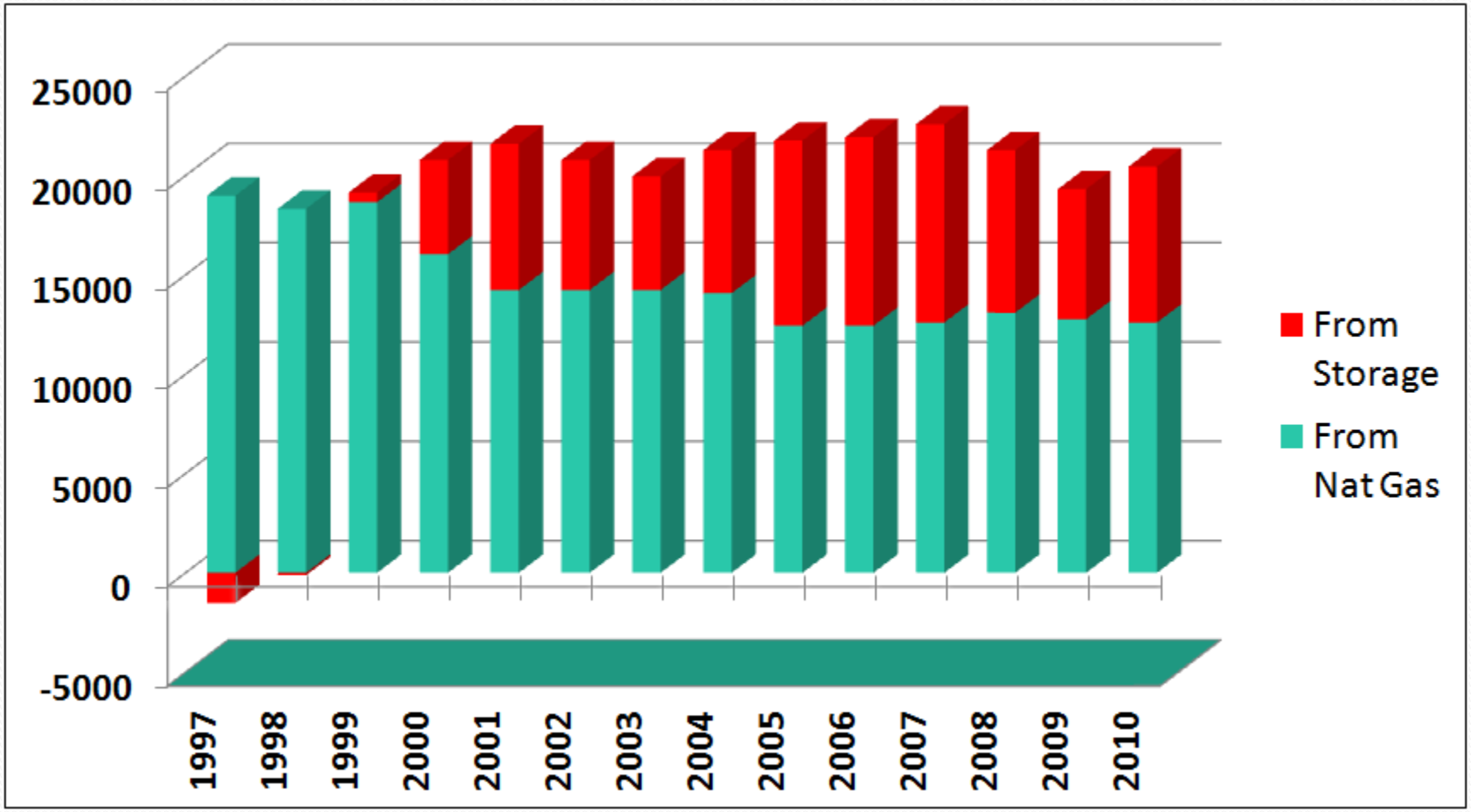
US He Production from Natural Gas Wells and Government Storage



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Estimated He Reserves

- **Total US reserves ~20.6 billion m^3**
  - **Economically Recoverable now ~4 billion m^3**
  - **~ 17 billion m^3 in low grade reserves**

- **As economical reserves are depleted, marginal sources will come into play**
  - **Marginal reserves can be accessed with advanced technology**

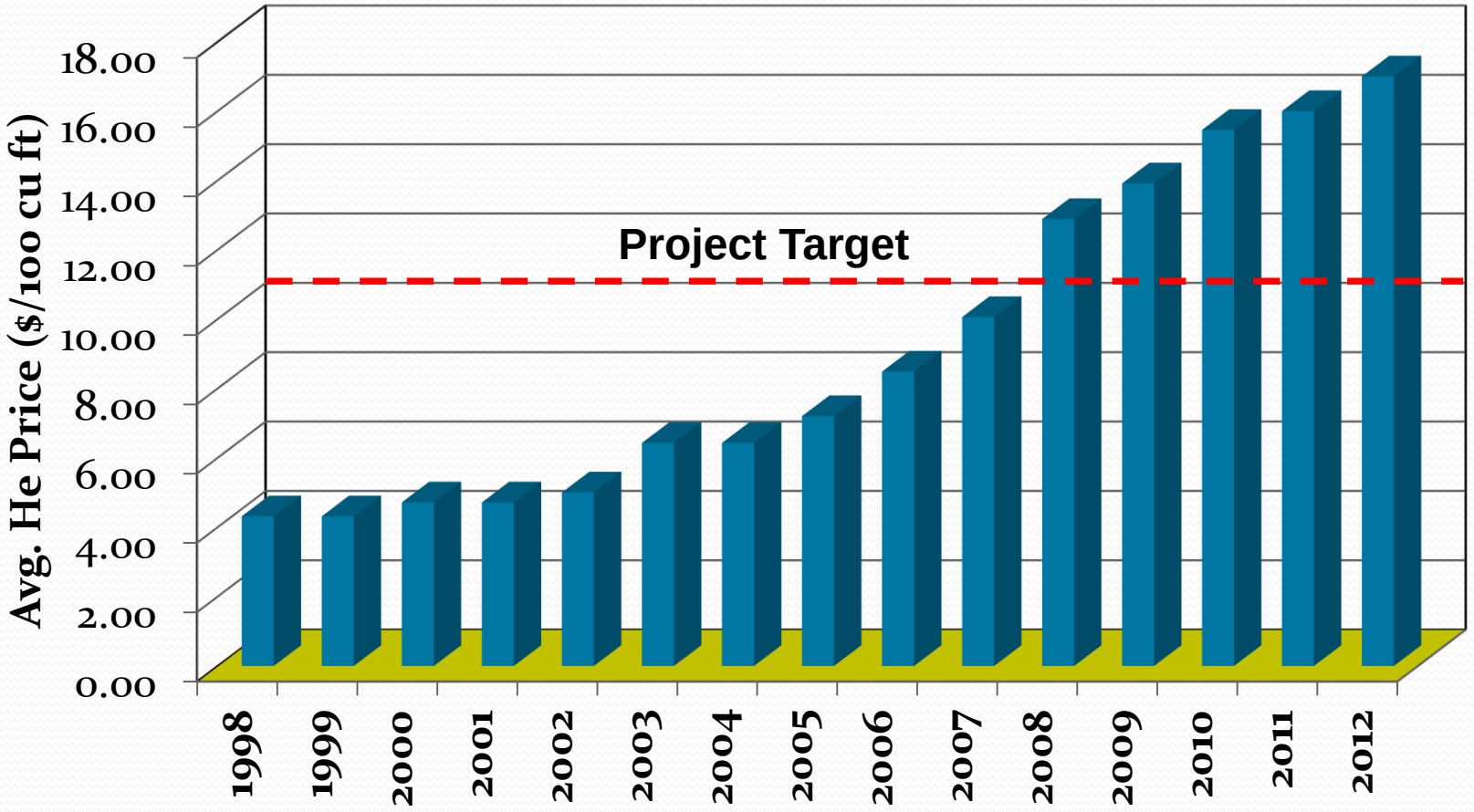
Current Project

- **Objective:**
  - ***Develop a membrane hybrid technology which enables economic recovery of He from marginal fields containing concentrations, below today's "economic threshold".***
  - Phase II builds on the progress made in Phase I and is intended to lay the foundation for advancing the technology to field tests
- **Project Team:**
  - Helios-NRG, LLC – Prime
  - Oak Ridge Nat'l Lab
  - MTR
  - Praxair – Business/Marketing Advisory role

Technology Strategy

- Define feed gas
- Synthesize process cycles
- Use He price to set targets for development
- Develop new membranes with superior properties
- Develop advanced hybrid processes
- Test new membranes
- Refine economics
- Establish foundation for Phase III field demo

Average US Price of Grade-A He



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Setting Targets for Development

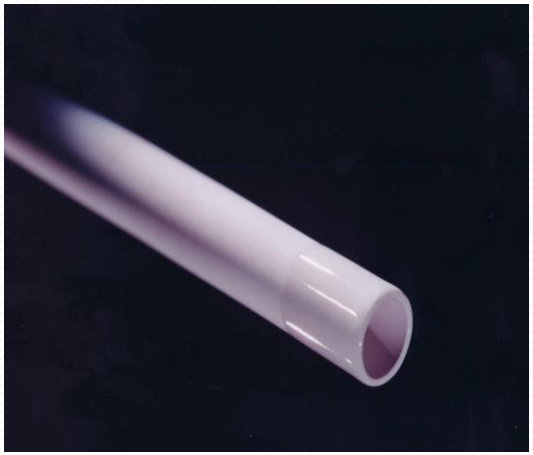
- **Typical raw gas from marginal wells is a mixture of several gases + small amount of He**
  - **Methane rich wells**
  - **Nitrogen rich wells**
- **Potential processes to recover He**
  - **Type A** – Mem + PSA process w/o cryo
  - **Type B1** – Cryo + Mem + PSA
  - **Type B2** – Adv cryo + Mem + PSA

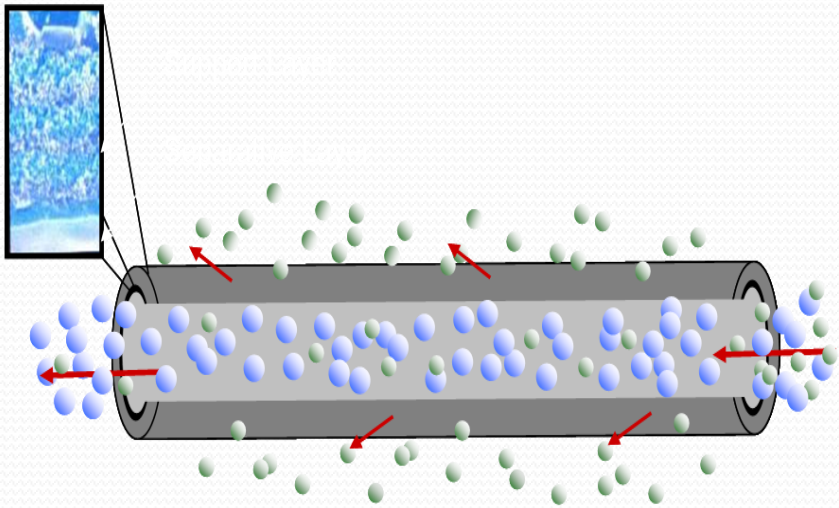
Membrane Development

- **Advanced sieving membranes at ORNL**
  - Separation based on molecular size
  - Applicable to both CH_4 and N_2 rich fields
  - Not limited by the Robesson upper bound for polymers
  - Not plasticized by HC or CO_2
- **Improved polymeric membranes from MTR**
  - Commercial mfg. process & module design
  - Membrane optimized for current separation
  - Low cost

ORNL Sieving Membrane's

- Pore diameters of < 1 nm to 5 µm
- Thin wall support structure and membrane layer made of variety of metals and ceramics
- 300 and 400 series Stainless Steel, Hastelloy X, iron-aluminide





- Membrane layer
  - Al_2O_3, γ-Al_2O_3
  - ZrO_2,TiO_2, SiO_2
  - Carbon, zeolite
- Best pure gas properties:
  - Selectivity >85
  - Permeance > 150 GPU

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Gas Separation with Carbon Membrane

✓ **Molecular Sieve Carbon Membrane (2.5-5.5 Å)**

Efficient for the separation of gas mixture with similar molecular size:
He/N_2, O_2/N_2, CO_2/N_2, CO_2/CH_4

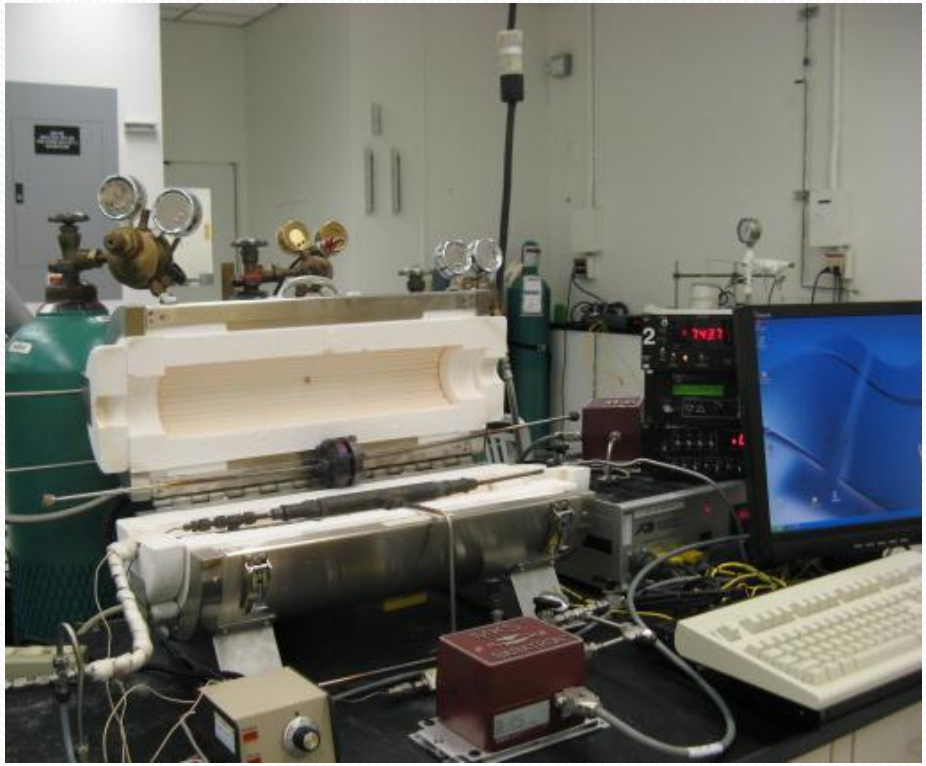
✓ **Activated Carbon Membrane (8- 20 Å)**

Efficient for the separation of non-condensible gas (N_2, O_2, He, etc.) and condensible gas (hydrocarbon, VOCs, etc) mixture

Preparation of Carbon Membranes

Polymer precursor	✓ Phenolic resin
Preparation of Support	✓Porous metal composite support
Oxidation	✓ Gas phase oxidation
Pyrolysis	✓ Carbonization
Supported carbon membrane	✓ Permeation Test

ORNL Lab Facilities



High Temperature Gas Permeation and Separation

High Temperature Membrane Treatment

High Performance ORNL Membranes

Sample number	N2 permeance (GPU)	He permeance (GPU)	Selectivity
1749-61	2.6	142.5	54
1749-56	1.1	81.7	74.3
1749-68	1.7	100.1	60.7
1749-65	1.9	57	30.5
1748-61-1	1.5	85.4	55.4
1749-66	3	142.5	48
1479-70	1.3	107.3	81.3
1749-48	2	74.8	37.8
1749-71	3.1	90.1	29.3
1749-69	1.4	81.7	57.2
1749-72	3	68.5	23.1
1749-62	1.9	106.8	57.1
1749-58	1.8	155.2	88.2

* GPU = 1 x 10^{-6} $cm^3/(cm^2\text{-s-cm Hg})$ at 25 ˚C

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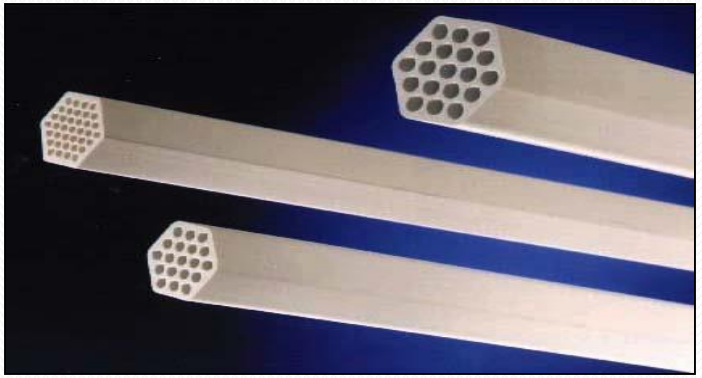
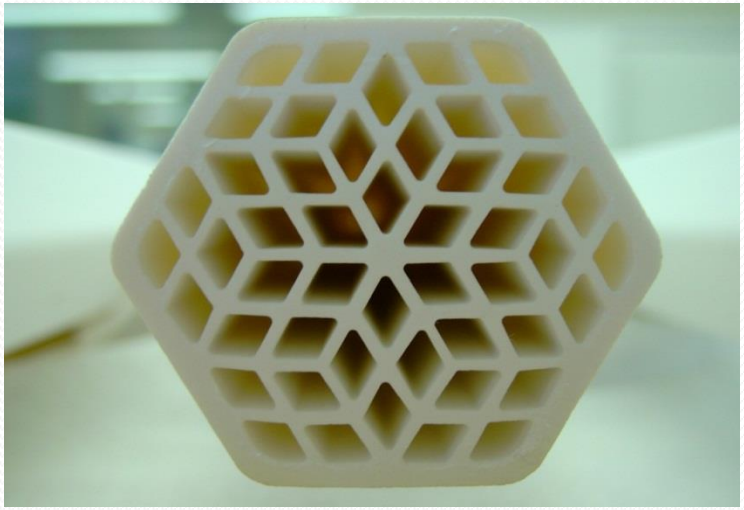
Options for Membrane Scale-up

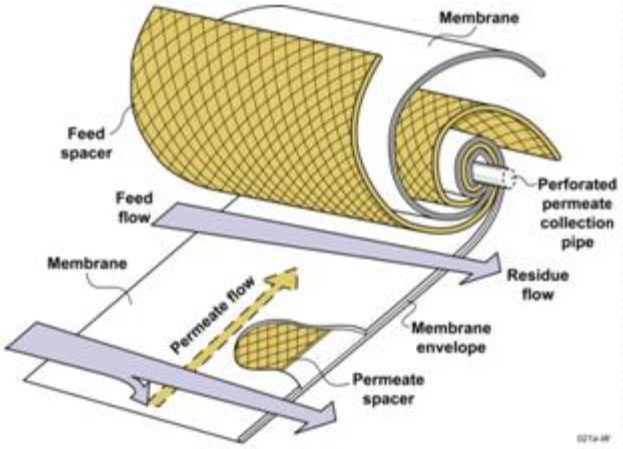
- Membrane supports
  - Tubular (shell/tube)
  - Hexagonal multichannel
  - Circular multichannel
  - Honeycomb monolith



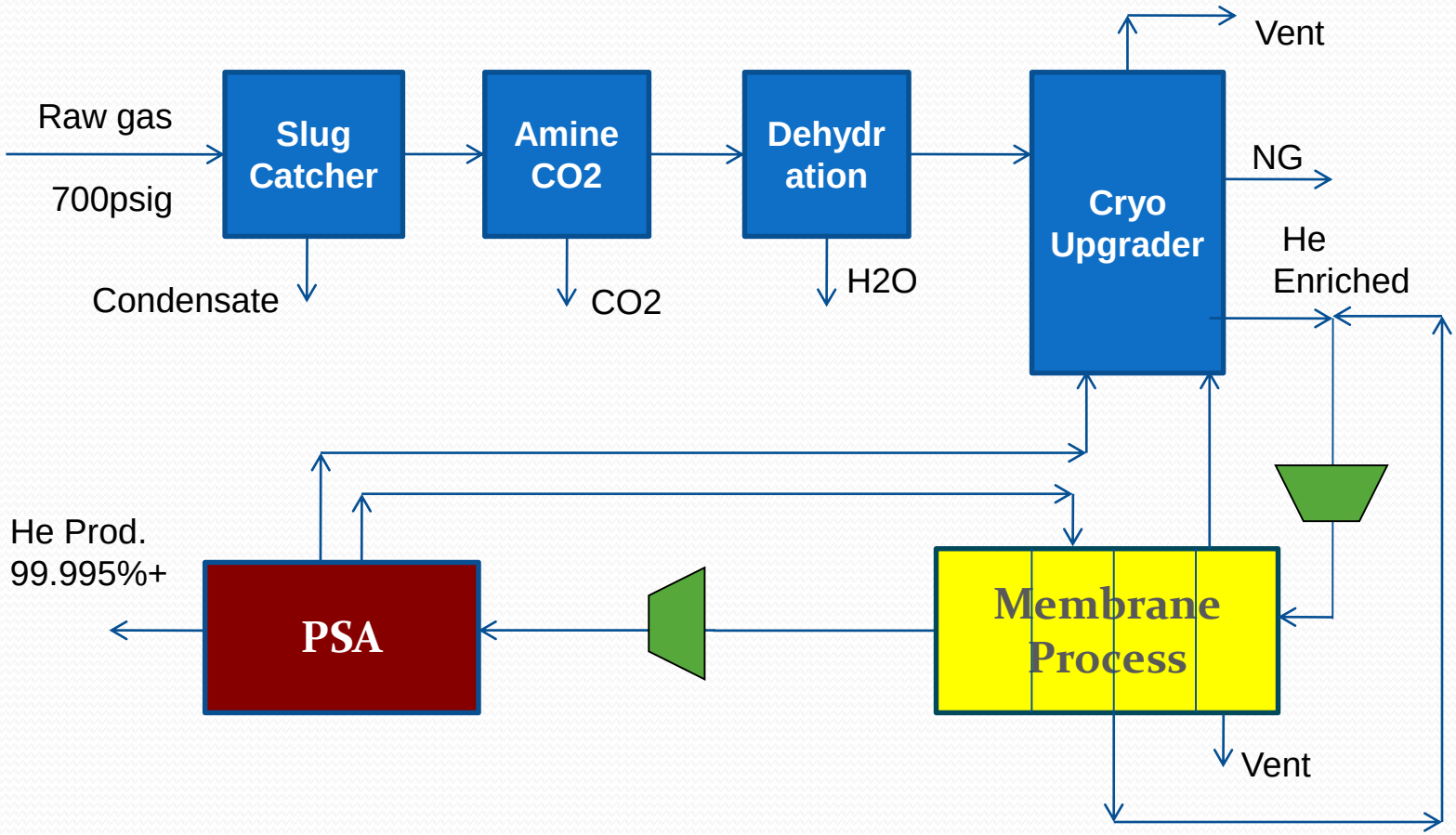


MTR Membrane's

- Polymeric membranes
- Choice of many polymers
- Spiral wound design
- Fouling resistant
- Low pressure drop
- Excellent for roughing stage
- Pure gas properties exceed target
  - Selectivity 30% higher
  - Permeance 38% higher



Advanced Hybrid Process for Type B

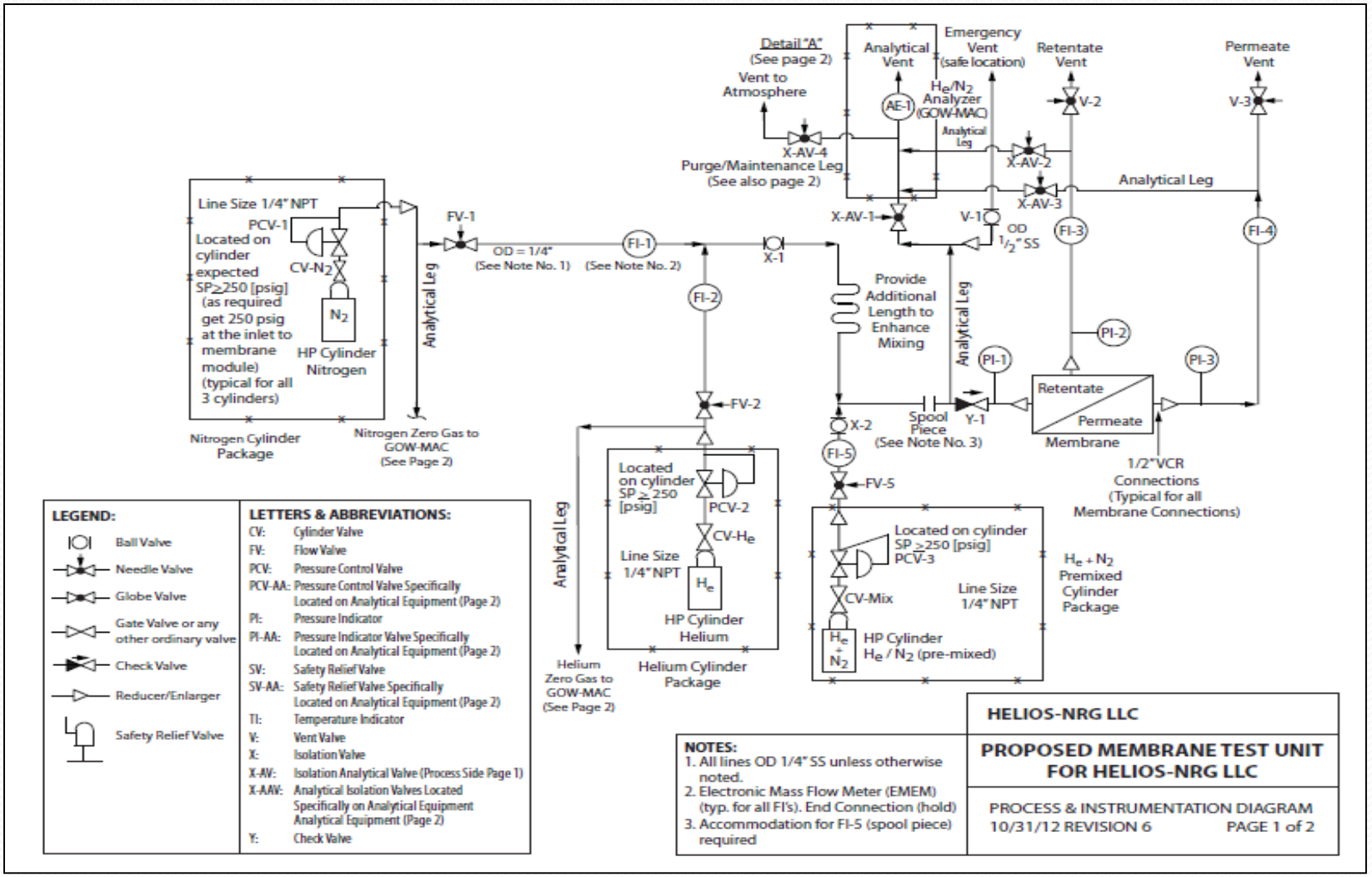


Lab Pilot Unit

MTR

ORNL

Pilot Plant P&ID



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Lab Pilot Unit

- Project objective was to test membranes **at B2 process conditions using mixed gas**
- Praxair Inc has donated He and specialty mixtures for tests
- Very successful startup
- Modules received from MTR and ORNL
- MTR tests complete
  - **Tests were completed for both B1 & B2 processes**
  - Successful mixed gas tests
- ORNL tests underway
- Plan to conduct some Process A tests as well

Process Economics from Process Tests

- **Advanced hybrid process improves economics by ~20%**
- **This combined with the better-than-plan membrane properties enabled much superior process economics**
- **Application Type B2 – Target Exceeded (Phase 2 Objective)**
  - ~25% better than our goal
- ***Application Type B1 – Target met***
  - ~15% better than goal
- ***Application Type A - Likely possible***
  - To be evaluated in future

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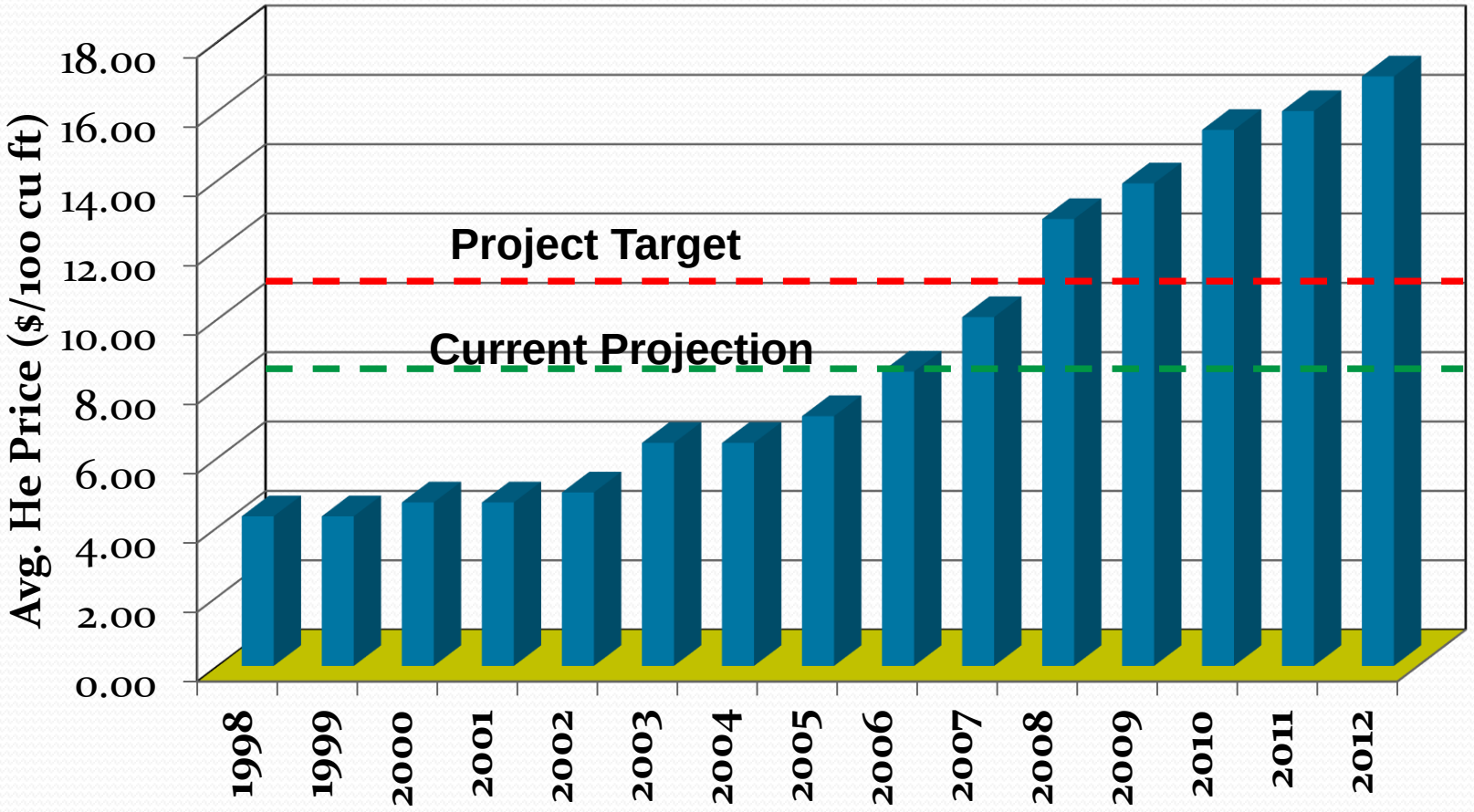

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Summary

- **ORNL membrane selectivity 6x of target**
- **Hybrid process with much improved economics developed**
- **Pilot unit built, process tests nearing completion**
- **Projected economics greatly exceed Phase2 goal**
- **Expect to achieve/exceed all Phase 2 objectives**
- **Developing Phase 3 plans**

Thank You!

About Helios-NRG

- **A technology company founded in '09 by ex-Praxair personnel**
- **Consulting**
  - Industrial Gases, Separations, Clean Energy, Carbon Capture, Gasification, Adv. Technologies, and Business Dev.
- **Technology Development**
  - Advanced separations
  - Membrane Technology
  - Algae Biotechnology for carbon capture/utilization & water remediation