Membrane/Module Scalability Manufacturing and Other Challenges

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Introduction to MTR

- Privately-held, 90 employees
- Started in 1982, initially funded by SBIR grants
- Developed membrane materials and commercialized products in petrochemical, natural gas and refinery industries
- Provides complete turn-key solutions with about 300 membrane systems installed worldwide
MTR designs, manufactures, and sells membrane systems for industrial gas separations

**Petrochemicals:** Propylene/Nitrogen

**Hydrogen (Refinery):** $\text{H}_2/\text{CH}_4$, CO, CO$_2$

- **Natural Gas:**
  - Fuel Gas Conditioning
  - $N_2$ Removal
  - $H_2S$ Removal
  - CO$_2$ Separation

- **MTR Product Lines**
  - 20 Years of Commercial Success
  - A Leader in Membrane and Process Design
  - Over 100 Patents on Membrane Technology
  - Over 300 References in Various Applications Worldwide
Membrane Classifications

Size Selective

Small molecules pass through

Solubility Selective

Big molecules pass through

Feed - high pressure

Permeate - low pressure

Slow
C_4^+
C_3
C_2
C_1
CO
N_2
O_2
CO_2
H_2
Fast

Size Selective Membrane

Slow
N_2
H_2
O_2
CO
C_1
C_2
C_3
C_4
CO_2
C_6
H_2S
Fast

Solubility Selective Membrane
Membranes have to be thin to provide useful fluxes.

Gas Separation Membranes Have Asymmetric Structures

- Protective coating layer
- Selective layer: 1,000 Å thick
- Gutter layer
- Support membrane

Dense skin layer (0.1-5 µm)

Microporous support layer (50-100 µm)
Membrane Module Designs in Current Use

Capillary Fibers

Hollow Fine Fibers

Spiral-Wound Modules

Plate-and-Frame Modules
# Commercial Membrane/Module Development
(Concept to Commercialization)

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Example 1 - Membrane Development
Pd-Alloy Membranes for H₂ Separation

- Scaled Up Worcester Polytechnic Institute’s Pd-Alloy membrane technology for H₂ and CO₂ separation from coal/biomass-derived synthesis gas.

- Designed, fabricated skid, and supported field tests from 2011-2015 at NCCC, Alabama.

- Operated up to 450°C.

- Single or multi-tube membrane modules designed and tested.

- 2 – 10 lb/day of H₂ separated at >99.99 vol%.
Example 1 – Membrane/Module Development
Pd-Alloy Membranes for H₂ Separation

• Current Status (Early Stage)
• NCCC Field test Showed Good Results
• Membrane Stability was established to meet stated goals
• Single Tube Membranes were scaled to Tube-in-Shell Design with Multiple membrane tubes.

• Scale Up Challenges
  Membrane Scale-up Challenges
  – Process of Membrane Manufacture is Established- Scalable
  – Substrate materials availability limited – May require custom development
  – Long term mechanical and chemical stability in process environments
  – Cost of Materials may be a big cost concern

Module Scale-up Configuration
  – Shell and Tube configuration – Manufacturing techniques well understood
  – High temp operations – Materials considerations
  – Catalyst addition – Membrane protection
  – Integrated heat management for membrane reactor design

• Demo Scale – 3 to 5 years from current status
• Market pull exists if membranes with sufficient performance and stability can be demonstrated.

• MTR has explored polymer membranes for these separations for >10 years (we know what doesn’t work)

• Ceramic Membranes offer better separation performance
Example 2 - Olefin/Paraffin Separations
Membrane/Module Development

- MTR established collaboration on zeolite-based tubular membranes.
- Laboratory mixture results and long term lab tests were encouraging.
- Full-length Pilot Scale modules have been successfully tested in lab. Commercial-scale module design has been vetted in lab tests.
- A large demonstration plant is being installed in a site for 6-12 month testing performance with real process stream.

Scale Up Challenges

**Membrane Scale-up Challenges**
Tubular Zeolite membranes already being manufactured in Commercial scale – Scale-up not an issue.
Membrane Stability with trace components – Long term effects unknown.

**Module Scale-up Configuration**
Shell and Tube configuration – Sealing issues
Example 3 – Large Area Applications
Module scale-up Large Area Requirements

Carbon Capture Applications

500 MWₑ plant requires one million m² of membrane
Low pressure high membrane packing density required
Membrane Plants of these Sizes Exist

The Ashkelon desalination plant

- 1.5 million m² membrane area

- 40,000 spiral-wound RO membrane modules
- 7,000 housings

Source: http://www.water-technology.net/projects/israel/
Example 3 – Large Area Applications
Module scale-up Large Area Requirements

Key Challenges

- Skid packing density
- Manifolding
- Footprint Minimization
- A sweep process
- Needs low pressure drop

Large area, compact module skids
Needs wide, straight channels on both sides of the membrane

Flat Sheet Plate and Frame modules are a Preferred Configuration
Module Packing Density
Scale-up to Larger modules

• **Year 1**
  - Footprint: 1ft x 2 ft
  - Modules: 20 m²

• **Year 2**
  - Footprint: 1m x 1m
  - Modules: 100 m²
MTR’s Approach to Large Compact Packing

A single 100 m$^2$ module element

50 Module elements connected to make a 5000 m$^2$ module
Membrane Module and Test System

Membrane Contactor with Vessel

Feed Direction

Sweep Direction

Test System
Scaled Modules and Demo System

Sweep module

Main skid
Summary

- MTR has developed and commercialized the use of membranes for various applications in the Gas, Refinery and Petrochemical industries and has over 300 industrial references all over the world.

- MTR has developed 5 different membrane types from Concept phase to commercial or semi-commercial phase.

- MTR has developed novel Membrane packaging into industrial size modules for commercial use.

- MTR can partner with companies and institutions in developing specific applications using MTR expertise in membrane scale-up, module design, and pilot testing for applications of industrial interest.