Liquid Membrane Immobilized in Durable Inorganic Matrix for CO_2 Separation

Wei Liu, Jian Zhang

Pacific Northwest National Laboratory
Richland, Washington
USA

Presentation at the AIChE Annual Meeting

Nashville, TN

Nov. 13th, 2009

PNNL-SA-70062

Pacific Northwest
NATIONAL LABORATORY

Acknowledgement

- PNNL colleague:

  Nathan Canfield

  Shari Li

  Garry McVay

  Larry Pederson
- Heron Scientific

  Seth Miller
- DOE Financial support

  Industrial Technology Program

  Adv Concepts/GH Gas Cptr/Sqtr&Clean Utilization/Coal (Garry McVay)

Pacific Northwest
NATIONAL LABORATORY

Objective for CO_2 Capture from Flue Gas

- Rugged membrane materials stable under flue gas conditions (CO_2, O_2, N_2, H_2O, SOx, NOx, trace amounts of hydrocarbons)
- Highly permeable membrane to cope with low P_{CO2} in flue gas
- High surface area packing density feasible for scale-up to large scale flue gas capture application

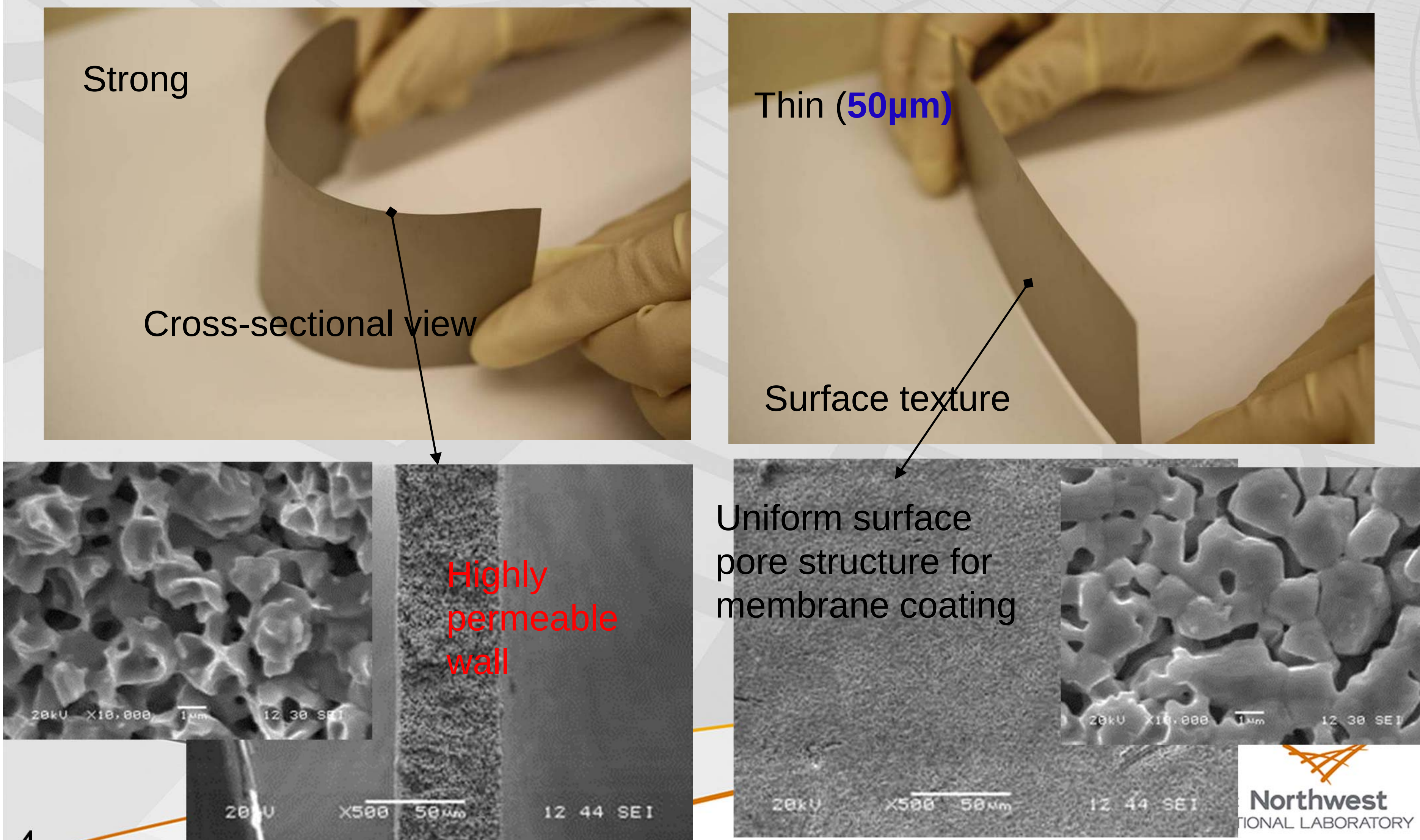
Estimate of membrane surface area needed for flue gas CO_2 capture

Coal combustion capacity, M T/Y	1.0	1.9	1.0	1.9
Power output, MW	250	500	250	500
ΔP of CO_2 partial pressure, bar	0.079	0.079	0.079	0.079
Permeance, mol/m^2/s/Pa	1.0E-07	1.0E-07	**1.0E-06**	1.0E-06
Membrane area required, m^2	2,671,503	4,942,281	267,150	494,228
Membrane packing density,m^2/m^3	1,000	1,000	1,000	1,000
Membrane module volume, m^3	2,672	4,942	267	494

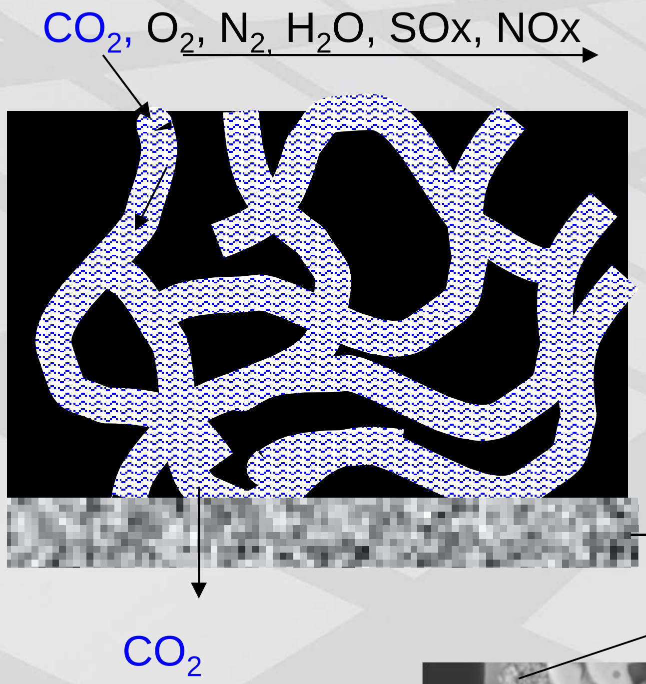
While certain CO_2/N_2 selectivity is necessary, high permeance is key for practical variability by reducing surface area, volume and cost.

Pacific Northwest NATIONAL LABORATORY

Our Technical Approach – planar metallic sheet-supported membranes (25-200µm)



Structure of immobilized liquid membrane in porous metallic sheet

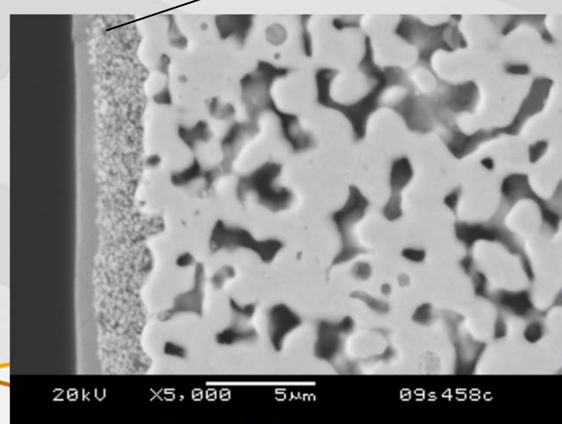


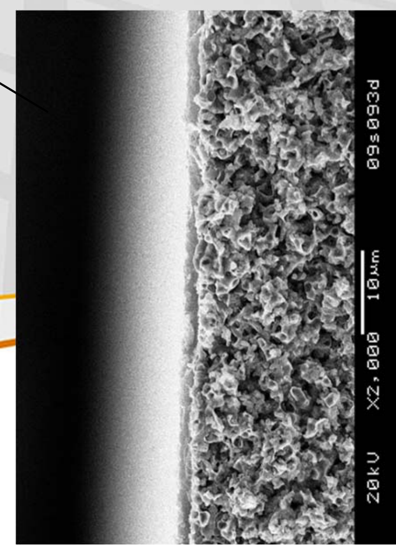
Attributes of liquid fluid:

- Selective CO_2 absorption
- Fast transport of absorbed/reacted C species
- Stable under flue gas conditions

$$\Delta P_c = \frac{2\sigma \cdot \cos(\theta)}{r_p}$$

Solution-impermeable barrier layer with tailored pore structures & surface properties





Key design Features of Proposed Membrane Sheet for Practical Application

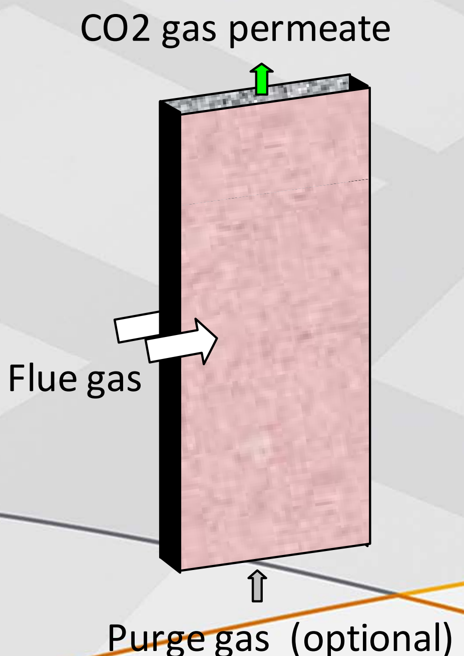
- Low pressure drop to withdraw permeate gas under vacuum
- Minimal pressure drop for flue gas to pass through
- Fouling resistance
- Easy installation and flexibility for replacement

Separation process economics:

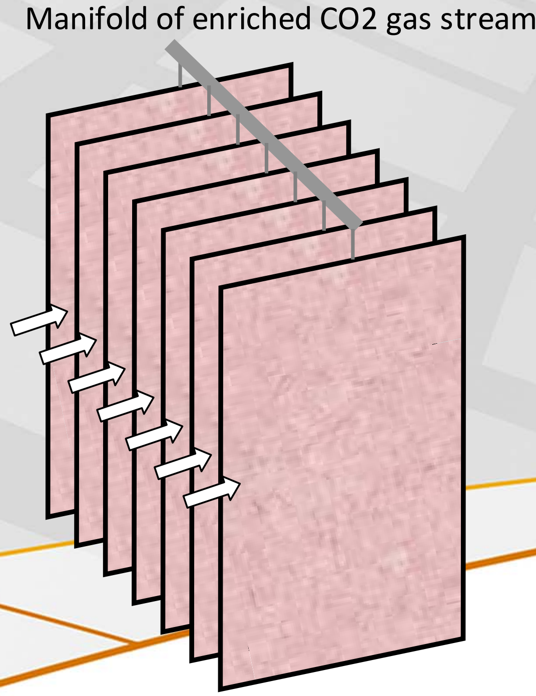
- Utilization of waste energy to pump CO_2
- ~10% consumption of coal energy
- Membrane cost ~¢0.6/(kW.h)

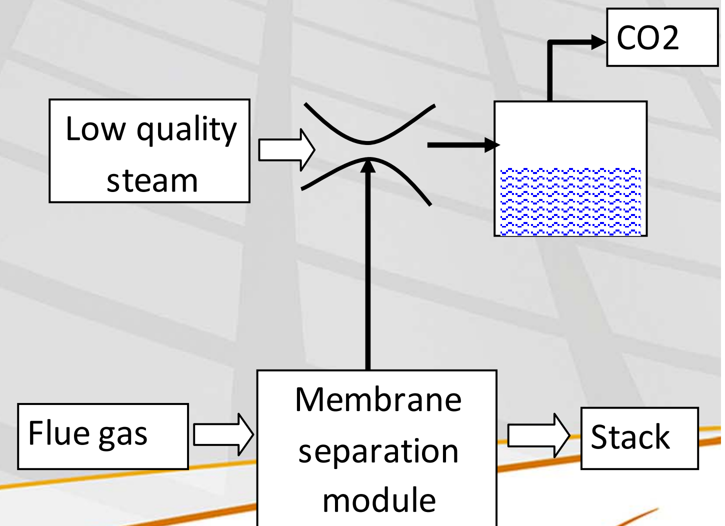
($100/m^2, 2-year life, 10^{-6} permeance)

Single membrane unit



Membrane module





Pacific Northwest NATIONAL LABORATORY

Present Membrane Design Principle - Facilitated CO_2 Transport

- CO_2 absorption selectivity and capacity is increased by coupling with a facilitator in the fluid

Step 1: reaction at G/L interface on feed side

$CO_2(g) + X(l) \rightarrow Y(l)$

Step 2: transport of Y across membrane

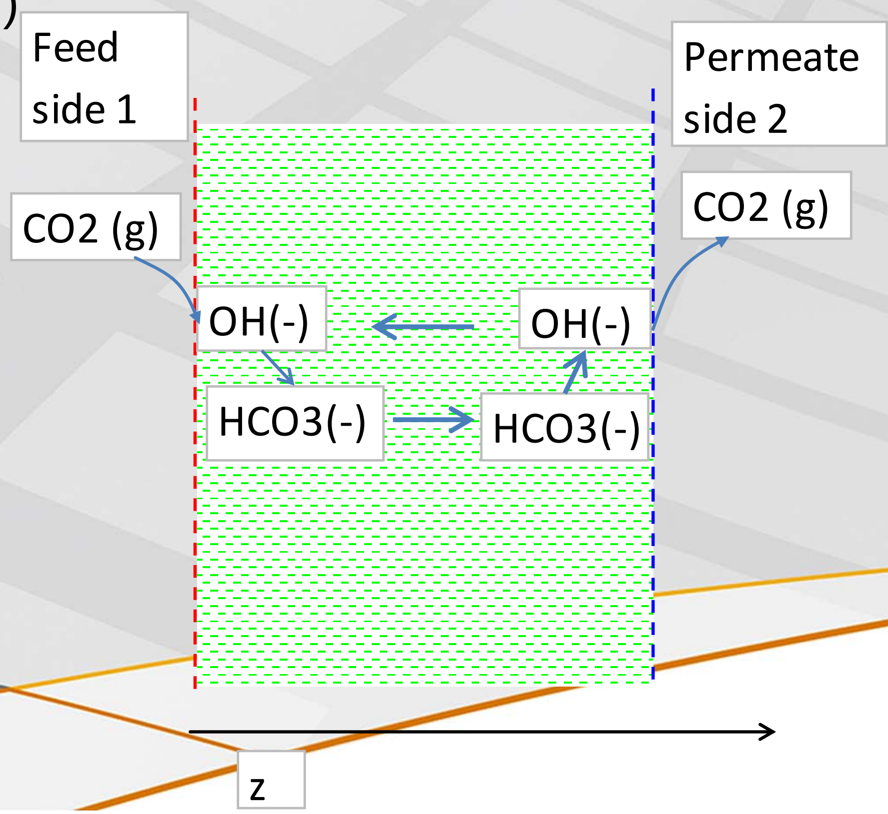
Step 3: reverse reaction at G/L interface on permeate side

$Y(l) \rightarrow CO_2(g) + X(l)$

Illustration with

$$X = OH^-$$

$$Y = HCO_3^-$$



Simplified Transport Equation by Assuming Kinetics-controlled Process

CO_2 permeation flux:

$P_1 = P_{CO2}$ in feed side

$$J = \frac{2C_0 \cdot k_{ad} \cdot P_1}{2 + 2 \cdot \frac{k_{ads} P_1}{k_{de}} + \frac{\delta \cdot k_{ads} P_1}{a} (\frac{1}{D_y} + \frac{1}{D_x})}$$

If desorption rate const far less than adsorption, flux is not affected by membrane thickness

$$J = \frac{2C_0 \cdot k_{ad} \cdot P_1}{2 \cdot \frac{k_{ads} P_1}{k_{de}}} = C_0 \cdot k_{de}$$

If adsorption rate const is very small

$$J = C_0 \cdot k_{ad} \cdot P_1$$

If diffusion coefficient is very small, either x or y,

$$J = \frac{2C_0 \cdot k_{ad} \cdot P_1}{\frac{\delta \cdot k_{ads} P_1}{a} (\frac{1}{D_y} + \frac{1}{D_x})} = \frac{2C_0 \cdot a}{\delta} \cdot \frac{D_x D_y}{D_x + D_y}$$

Pacific Northwest NATIONAL LABORATORY

Simplified Transport Equation
Assume fast absorption/reaction equilibrium at G/L interface

CO_2 permeation flux:

$P_1 = P_{CO2}$ in feed side

$P_2 = P_{CO2}$ in permeate side

$$J = \frac{2aKC_0}{\delta} \cdot \frac{P_1 - P_2}{\frac{2}{D_y} + (\frac{1}{D_y} + \frac{1}{D_x}) \cdot K \cdot (P_1 + P_2) + 2\frac{1}{D_x} K^2 \cdot P_1 \cdot P_2}$$

- Flux increases with decreasing membrane thickness, increases with concentration of the facilitator in the membrane, and increases with reaction equilibrium const.
- Diffusion of CO_2 complex (Y) or facilitation aid molecule (X) can become a rate-limiting factor.

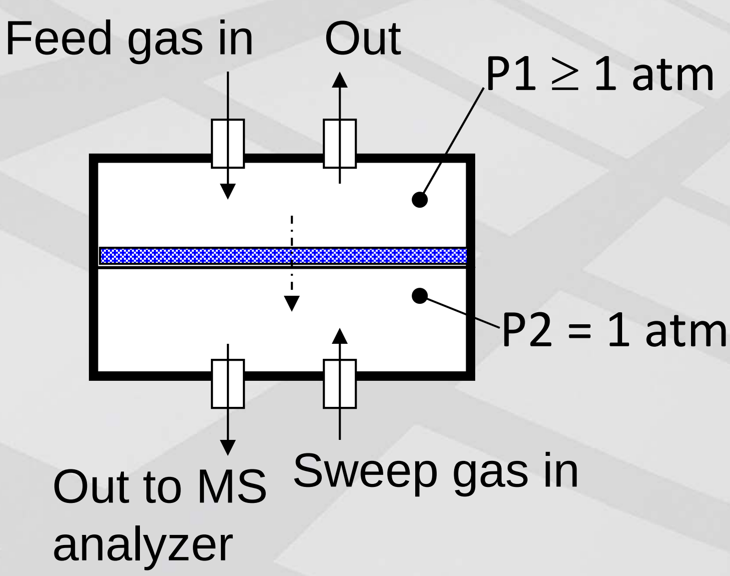
If K is very small

$$J = \frac{aD_y}{\delta} \cdot C_0 \cdot K \cdot (P_1 - P_2)$$

Pacific Northwest NATIONAL LABORATORY

Experimental Testing of Proposed Membrane Product Concept

Steady-state measurements with a feed gas mixture of known compositions



Permeance, mol/s/m²/Pa

$$P_i = \frac{F_i}{SA_m \cdot \Delta P_i}$$

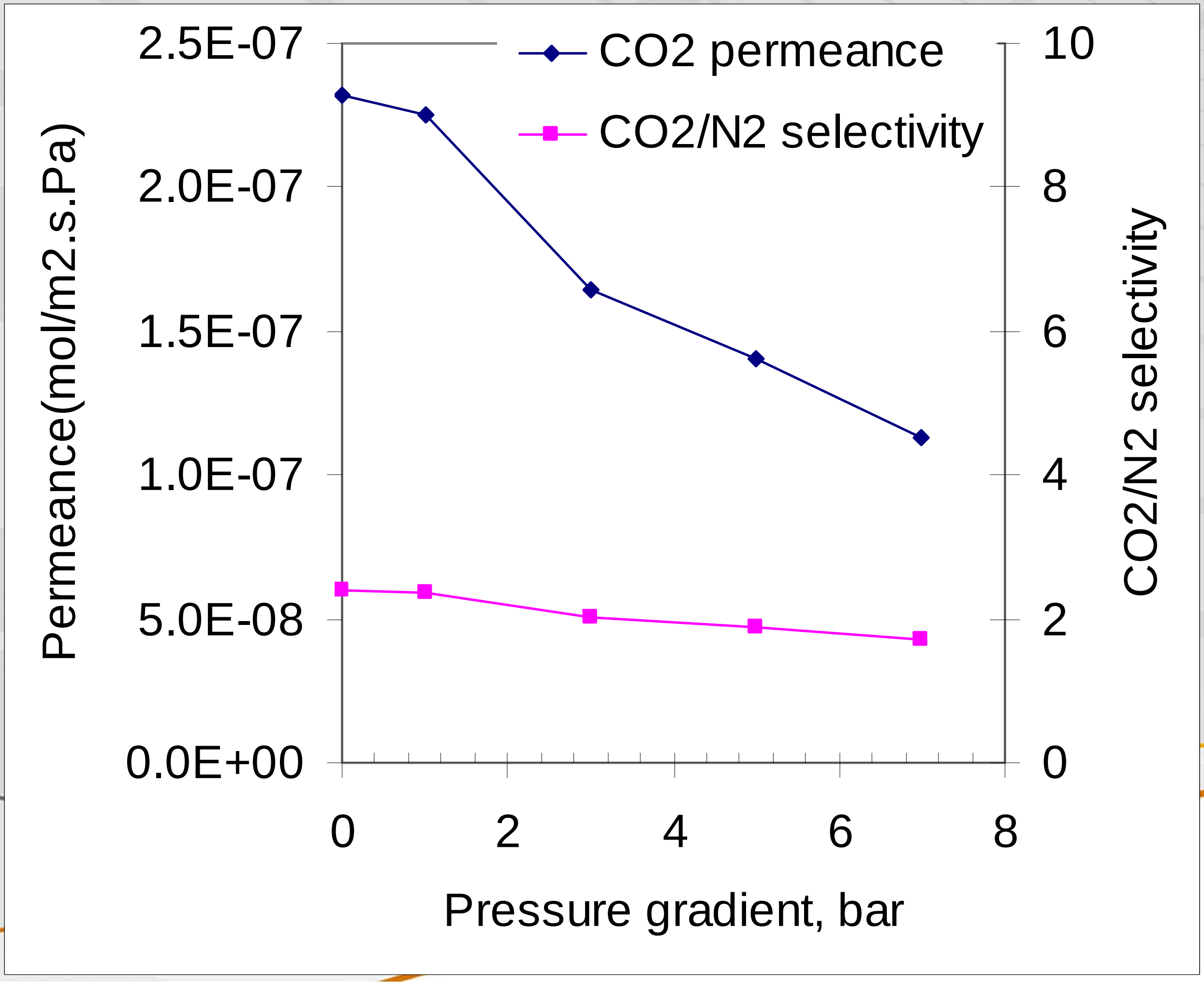
Selectivity factor

$$\alpha_{ij} = \frac{\left({y_i}/{y_j} \right)_{permeate}}{\left({x_i}/{x_j} \right)_{feed}}$$

CO_2 Permeability and CO_2/N_2 Separation of Ceramics/Metal Support Sheet (~50μm thick)

Feed gas composition: $CO_2/O_2/N_2$=15.3/5.3/bal, room temperature

- CO_2/N_2 selectivity is ~2 for dry feed gas and not affected by the feed pressure.

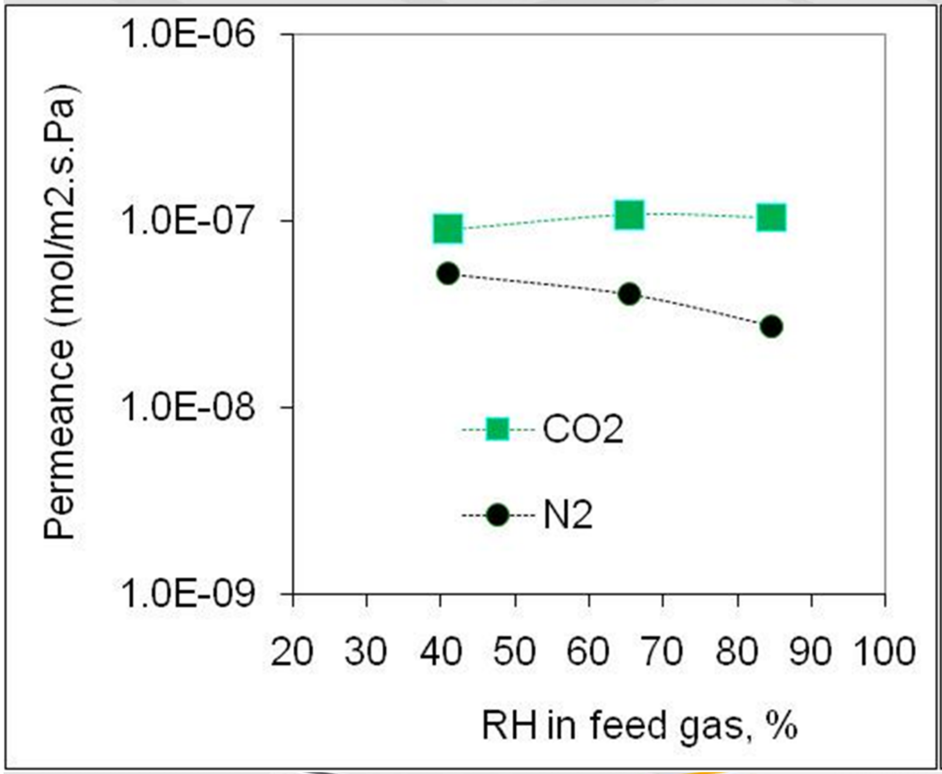


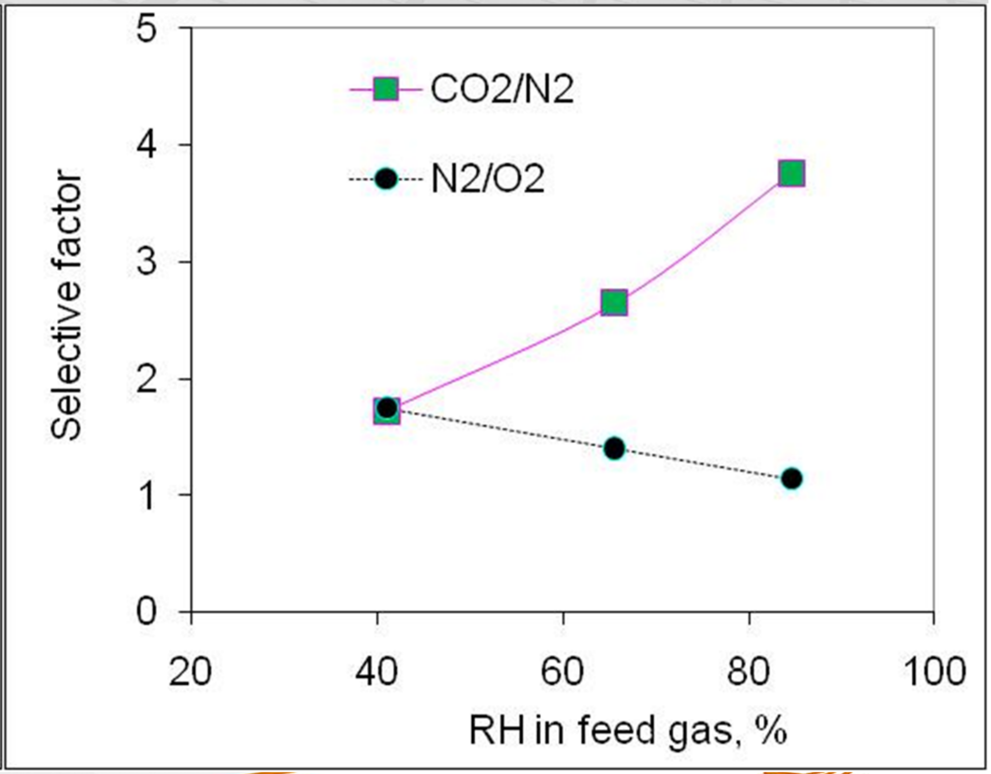
Pacific Northwest
NATIONAL LABORATORY

Impact of Humidity on Separation Performance of Ceramics/Metal Support Sheet (~50μm thick)

Feed gas composition: $CO_2/O_2/N_2$=15.3/5.3/bal, room temperature

- Humidifying the feed gas increases CO_2/N_2 selectivity but decreases CO_2 permeation compared to the dry gas.

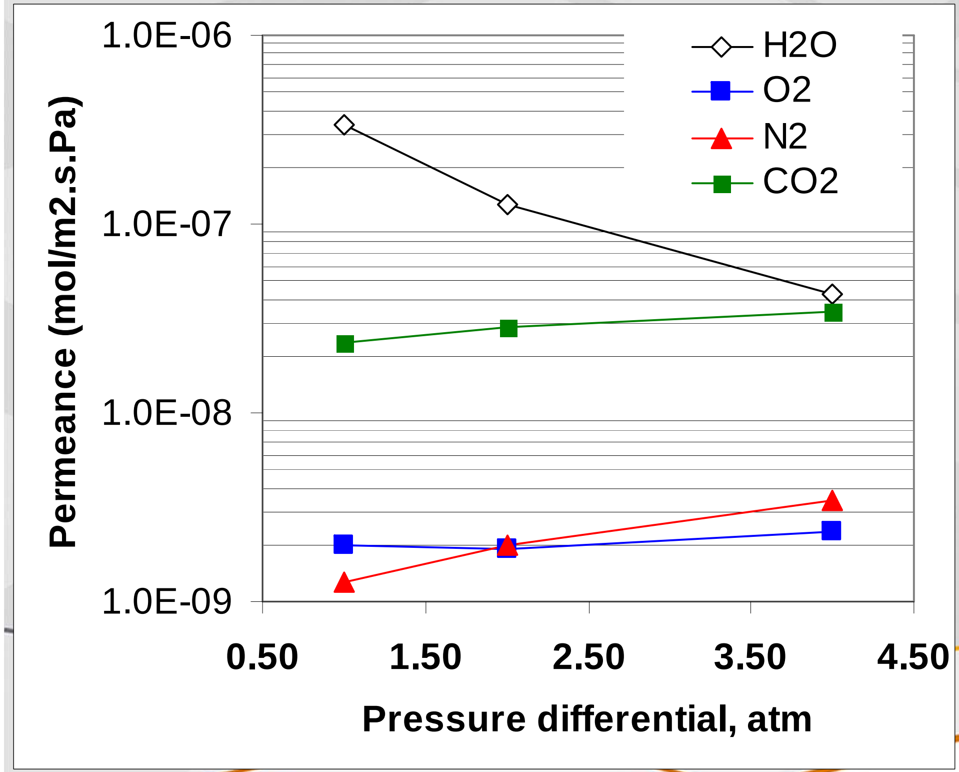


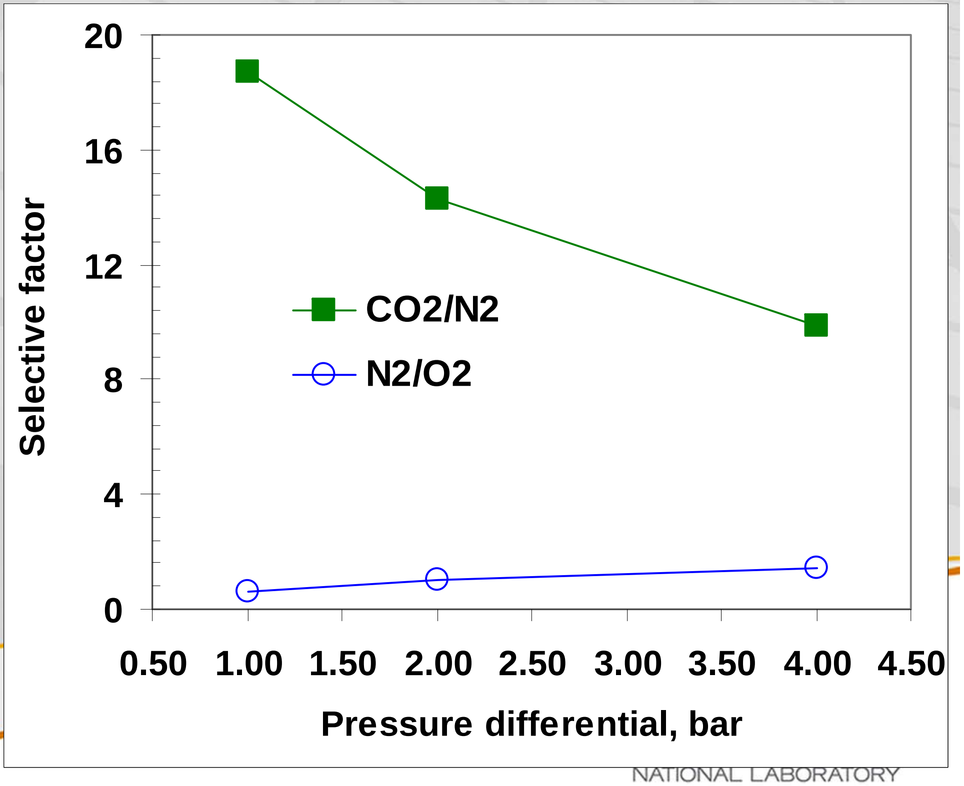


Aqueous Salt Solution Immobilized by The Ceramic/Metal Support Sheet (~50μm)

Feed gas: $CO_2/O_2/N2=15.3/5.3/bal$, 87% RH, room temperature

- Membrane showed stable performance in 87% RH
- Liquid was held within the pressure gradient tested
- Selective CO_2/N_2 separation is shown. Little N_2/O_2 separation, as expected.

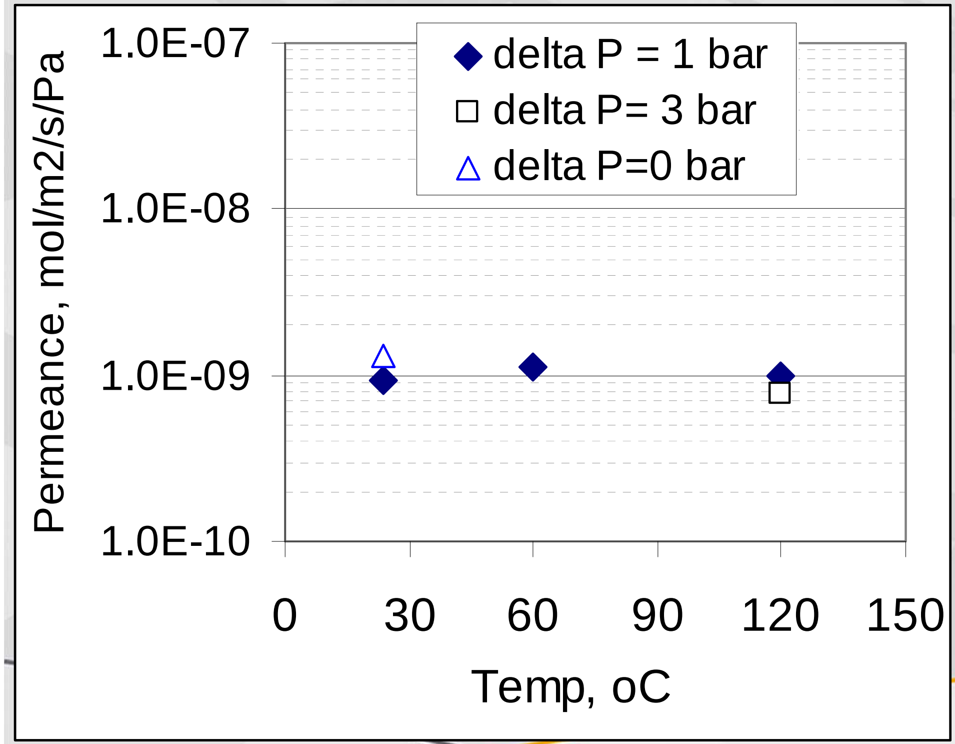


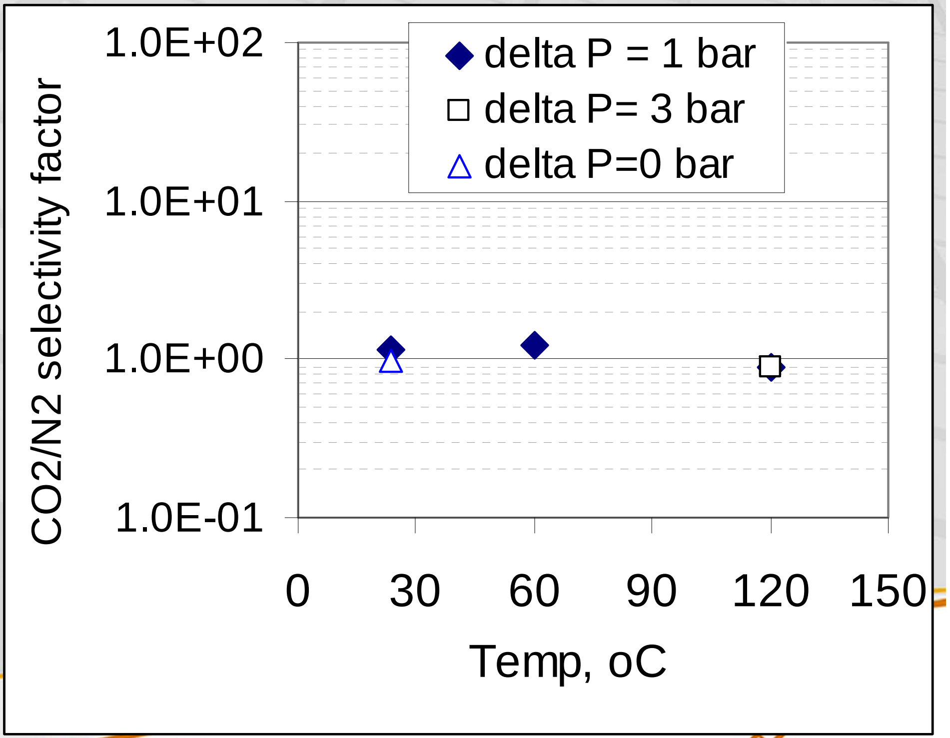


Ionic Liquid Salt Solution Immobilized in The Ceramic/Metal Support Sheet (~50μm)

Feed gas: $CO_2/O_2/N_2$=15.3/5.3/bal, 100% RH

- Ionic liquid reduces CO_2 permeation by 2 orders of magnitude but shows no CO_2/N_2 separation over a range of pressure and temperature tested

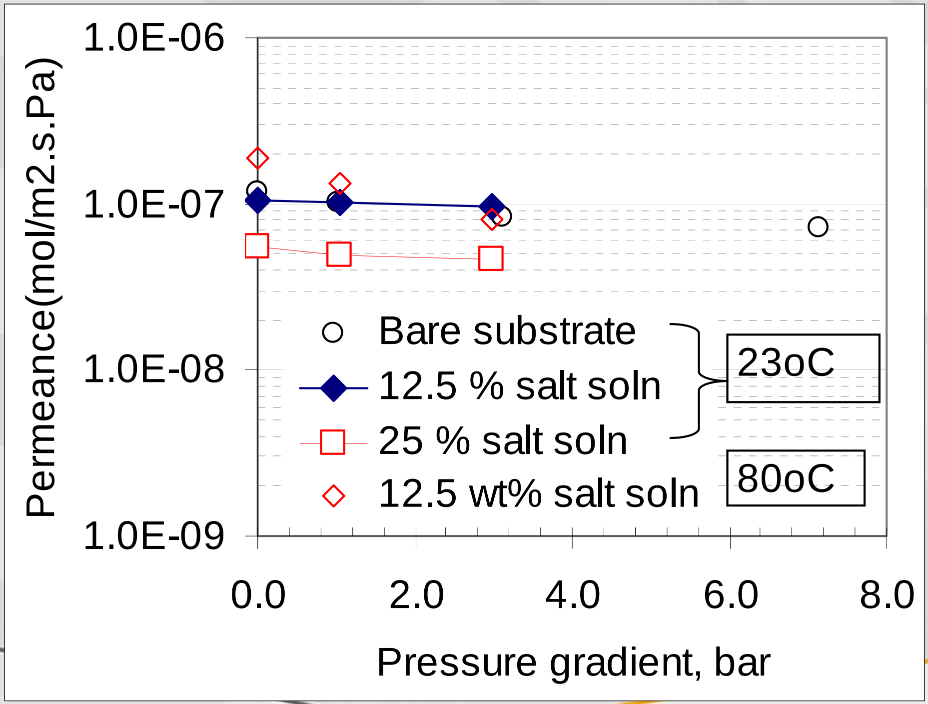


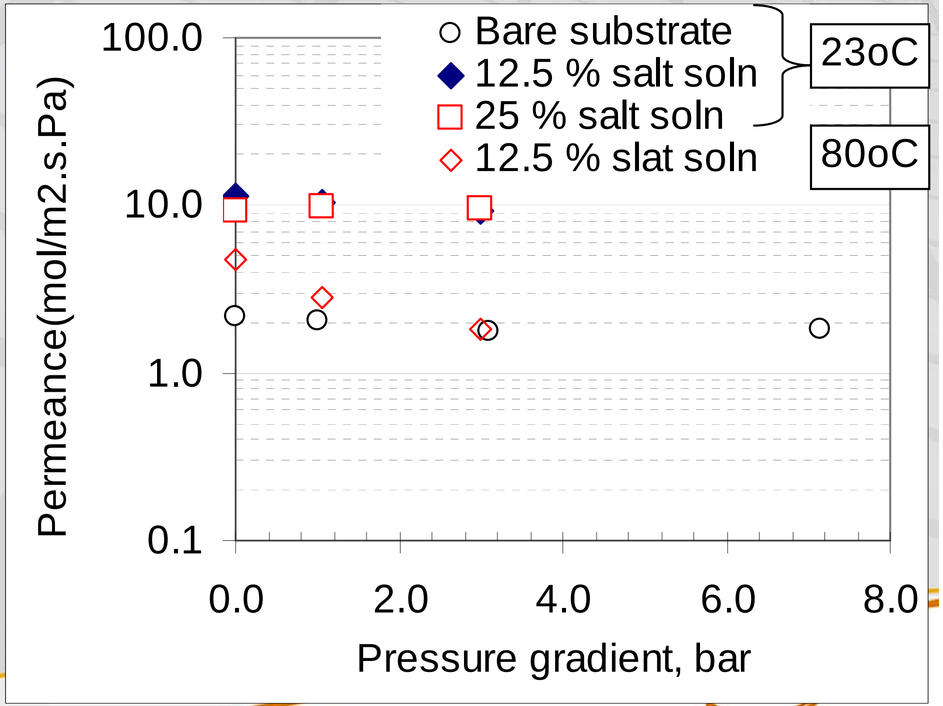


Pacific Northwest
NATIONAL LABORATORY

Sodium Glycinate Solution Immobilized in The Ceramic/Metal Support Sheet (~50μm)

- Loading of 12.5 % salt soln significantly increases CO_2/N_2 selectivity while CO_2 permeance stays same
- Doubling salt concentration decreases permeance while CO_2/N_2 selectivity stays same
- CO_2/N_2 selectivity decreases by raising separation temp



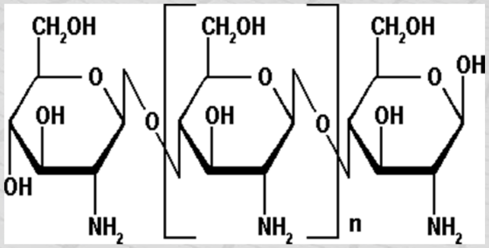


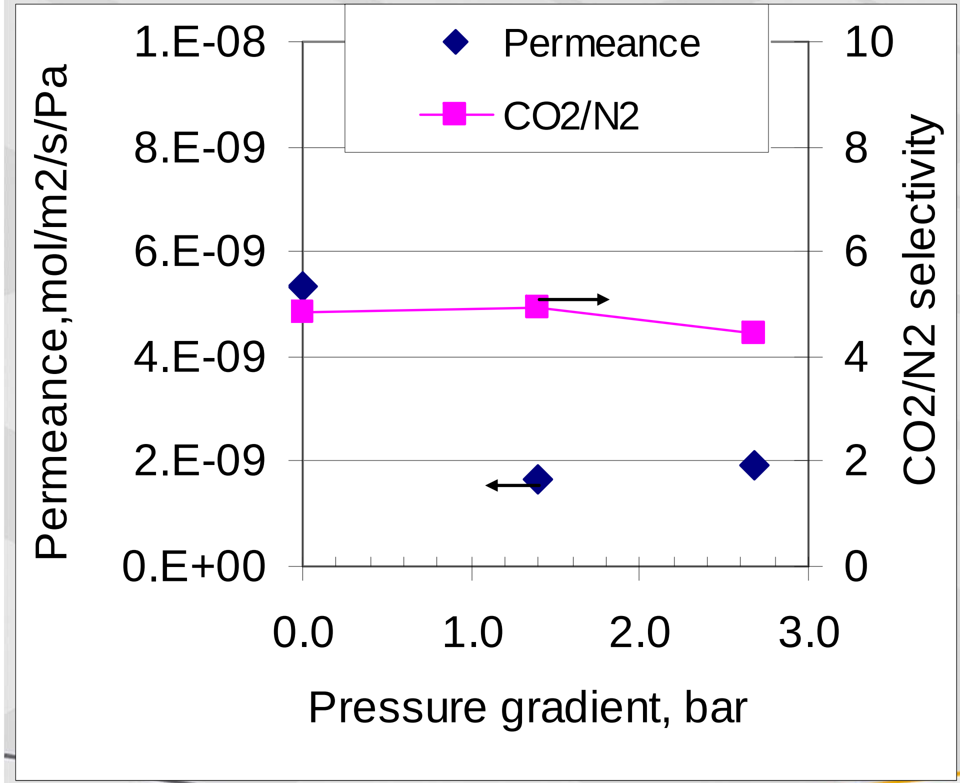
Feed gas: $CO_2/O_2/N_2$=15.3/5.3/bal, 71% RH

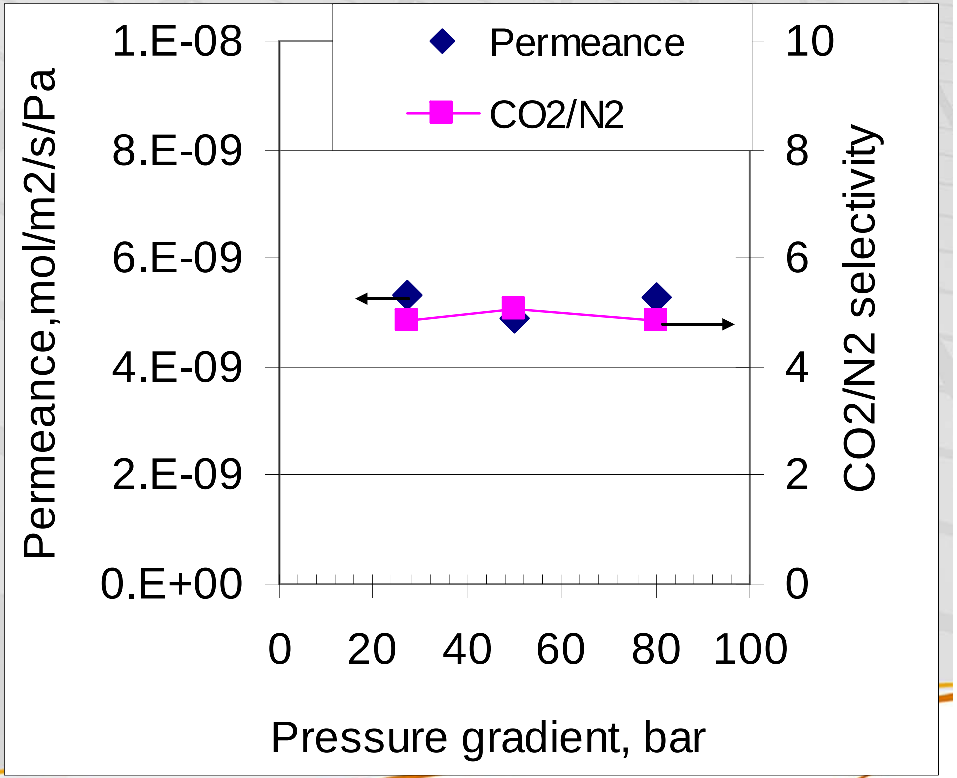
Pacific Northwest NATIONAL LABORATORY

Chitosan+Acetic Acid Solution Immobilized in The Ceramic/Metal Support Sheet (~50μm)

- Low permeation rate and low CO_2/N_2 selectivity





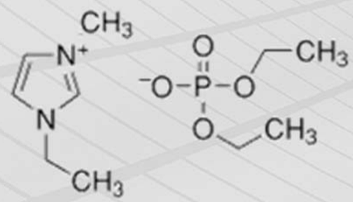


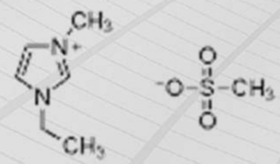
Feed gas: $CO_2/O_2/N_2$=15.3/5.3/bal

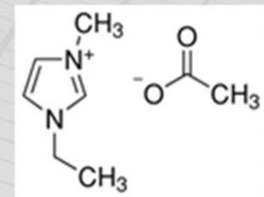
Pacific Northwest
NATIONAL LABORATORY

Amine-Containing Ionic Liquid Immobilized in The Ceramic/Metal Support Sheet (~50μm)

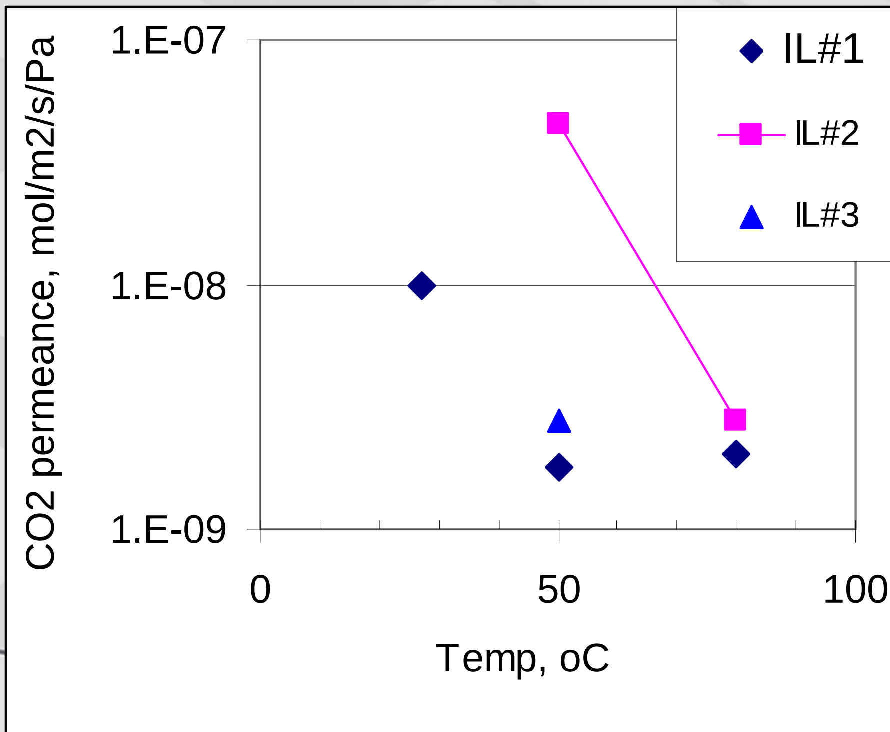
IL #1	[EMIM]acetate
IL#2	[EMIM]diethyl phosphate
IL#3	[EMIM]methanesulfonate

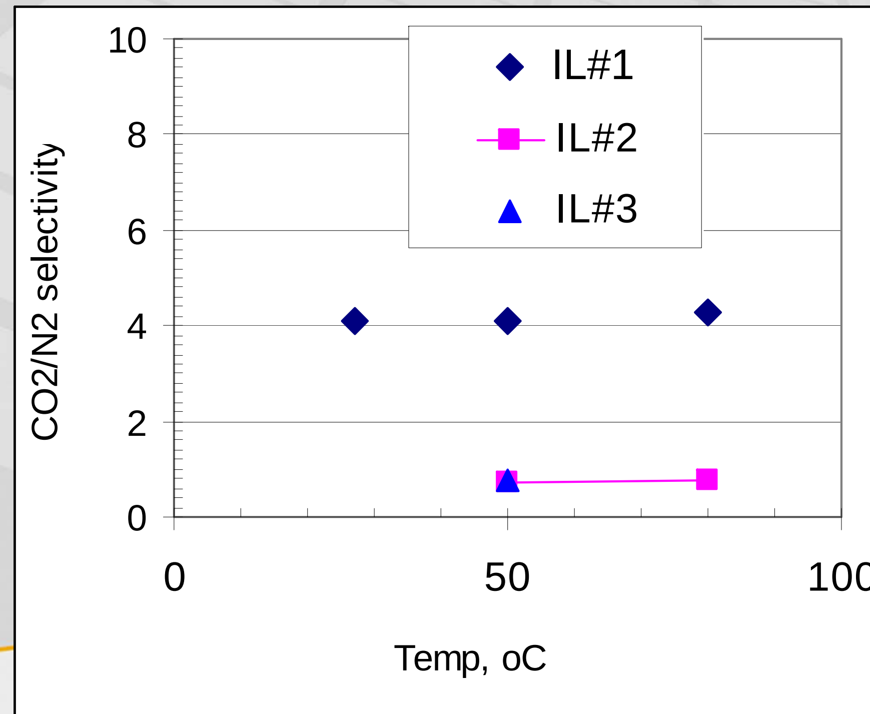






- Low CO_2/N_2 selectivity and low CO_2 permeance





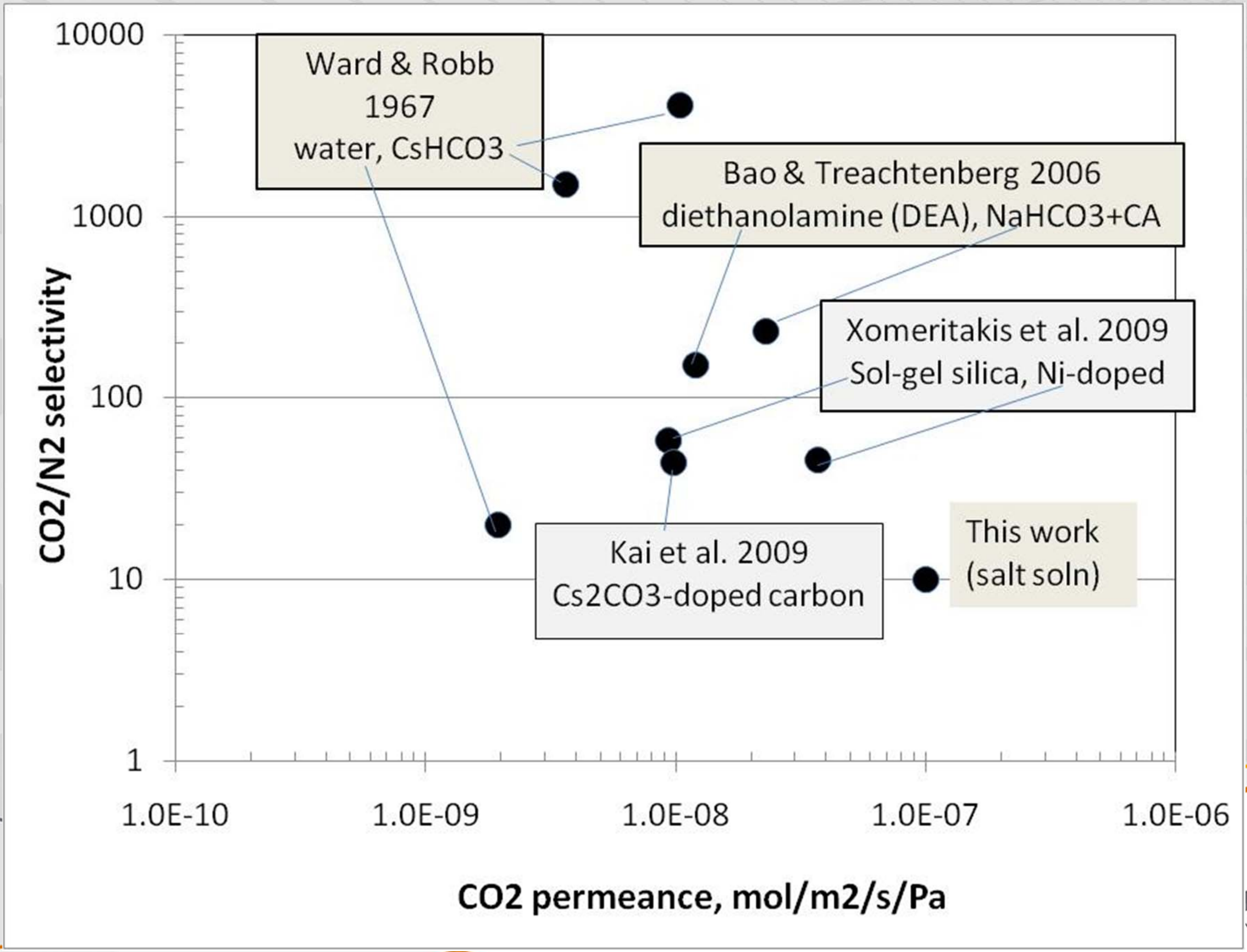
Feed gas: $CO_2/O_2/N_2$=15.3/5.3/bal, pressure of 1.7bar

Pacific Northwest
NATIONAL LABORATORY

Comparison of Present Membrane Product Design to Some Literature Reports ($H_2O/CO_2/N_2$)

Source	Support	Membrane
Ward & Robb. 1967. *Science*,156,1481-148	Porous cellulose acetate film (RO material), 70 μm thick/0.5mil of silicone rubber	• pure water • 6.4N $CsHCO_3$ solution • Saturated Cs bicarbonate + 0.5N sodium arsenite
Chen et al. 2001.*J. Mem. Sci*. 183, 75-88.	Hydrophilic polyacrylonitrile (PAN) fiber, 300μm (OD) x200 μm ID	• Pure glycerol
Bao &Trachtenberg. 2006. *J. Mem. Sci*. 280, 330-334.	Celgard micro porous polypropylene hollow fiber, 300μm (OD) x200μm ID	• 20 wt% diethanolamine (DEA) • CA (3g/cc)+$NaHCO_3$(1M)
Xomeritakis et al. 2009. *J. Mem. Sci*., 341,30-36	5nm-pore γ-alumina/Membralox tube	• Sol gel silica • Ni-doped sol gel silica
Kai et al. 2009. *J. Mem. Sci*., 342,14-21	150nm-pore α-alumina/Noritake tube	• Cs_2CO_3-doped carbon
This work	**Ceramics-modified porous metallic thin sheet (50μm)**	• **Aqueous salt solution**

Comparison of Different Product Design Concepts & Membrane Materials (CO_2, N_2, H_2O gas mix, ~1 atm)



Concluding Remark

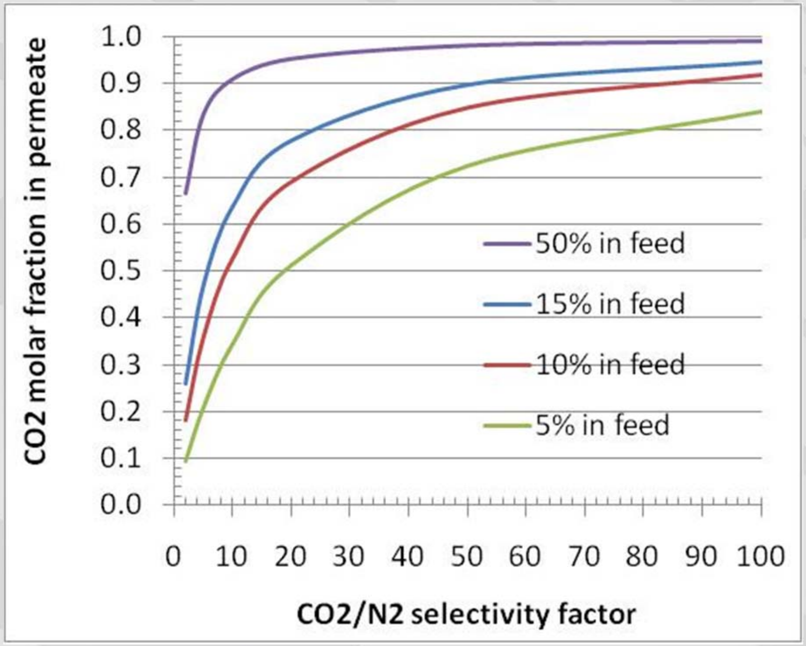
- It is feasible to construct a CO_2 separation membrane by immobilizing a CO_2-selective fluid on ceramics-modified porous metallic thin sheets:
  - Tolerate moisture in flue gas
  - Hold the liquid fluid at 4 bar of pressure differential tested (could be higher)
  - Achieve selective CO_2 separation by use of appropriate liquid fluids and substrates
- The proposed membrane design is of strong potential for large-scale production at low cost.
- Further work is ongoing to substantially enhance the permeance and selectivity by improving chemical and physical properties of the substrate, and by discovering better liquid fluids.

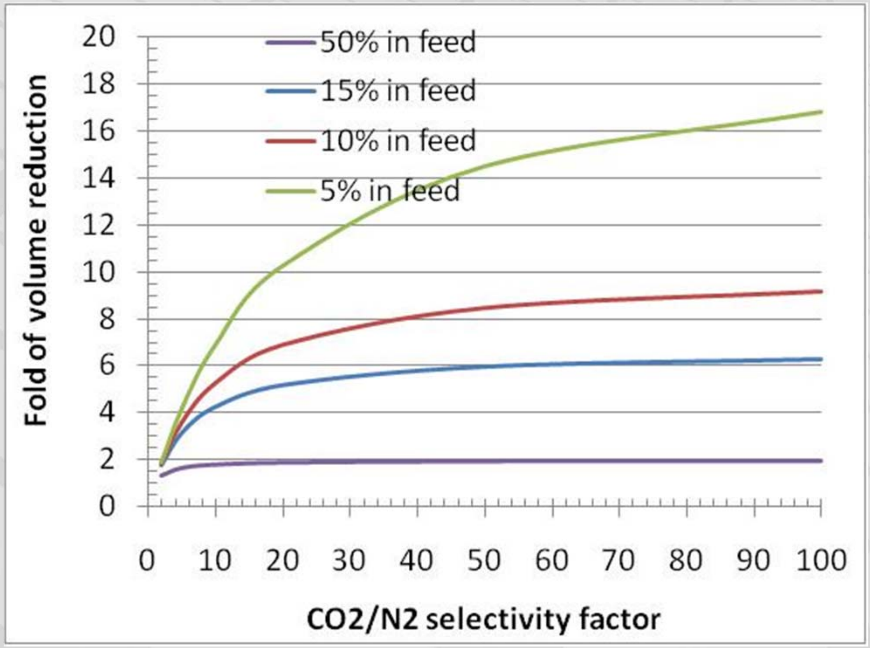
- Back-up slide

Pacific Northwest
NATIONAL LABORATORY

Impact of Permeance and Selectivity on Process Economics

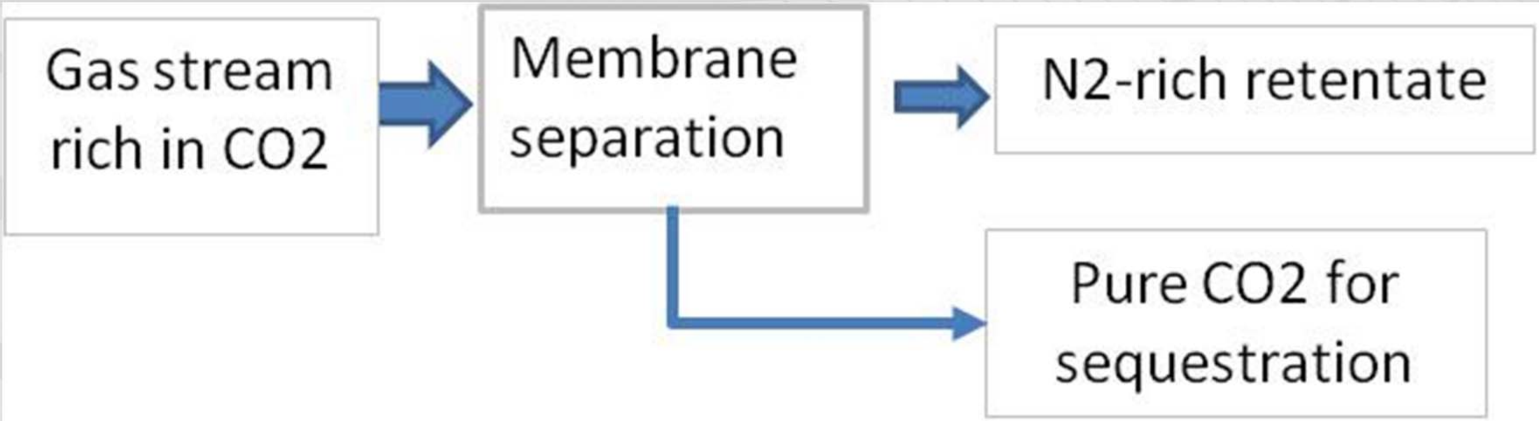
- Permeance directly correlates with membrane productivity and should be as high as possible.
- Impact of further increasing selectivity above a certain value becomes marginal

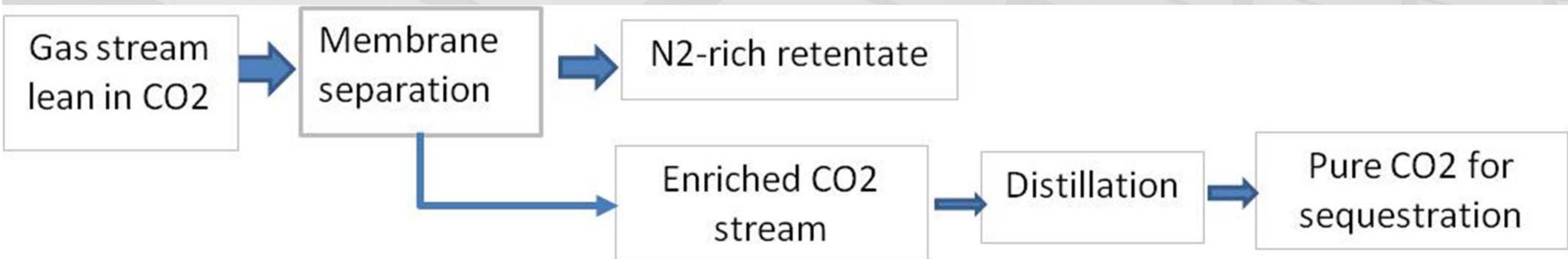




- It becomes impractical to concentrate CO_2 from very dilute gas to >95%
- Membrane may better serve a rough concentration process to reduce the gas volume by a few fold for other separation means, such as fractionation.

Pacific Northwest
NATIONAL LABORATORY





Pacific Northwest NATIONAL LABORATORY