CO_2 separation by FSC composite membranes and challenges in up-scaling of the membranes for pilot scale testing and industrial use

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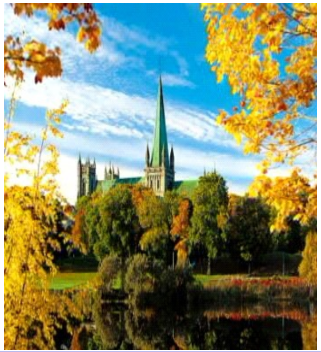


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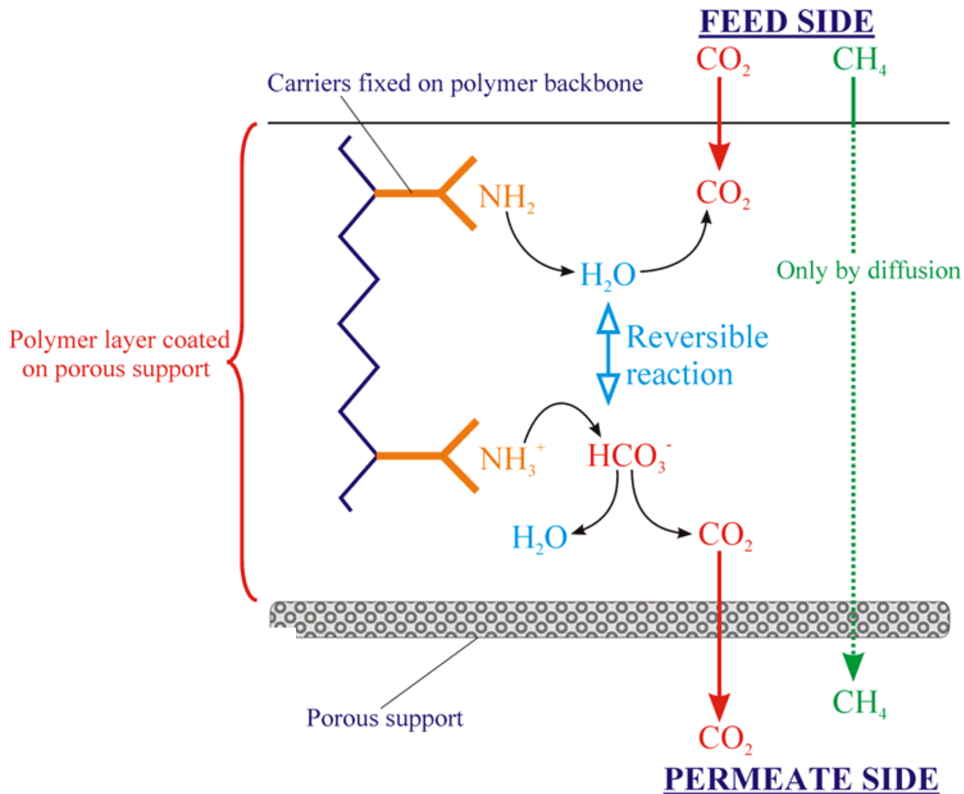
Outline of Presentation

- What is FSC membrane and brief development story
- Membrane performance result & status
- Lab scale development effort
- Up-scaling; flat sheet membranes
- Up-scaling; hollow fiber membranes
- Durability test
- Potential industrial applications & comparison with CO_2 absorption method
- Brief result of process simulation (feasibility suggestion)

Fixed site carrier (FSC) membrane principle



Flux of CO_2:

$$dQ_{CO2} = dA\frac{D_{CO2}}{l}(C_{CO2,0} - C_{CO2,l}) +$$

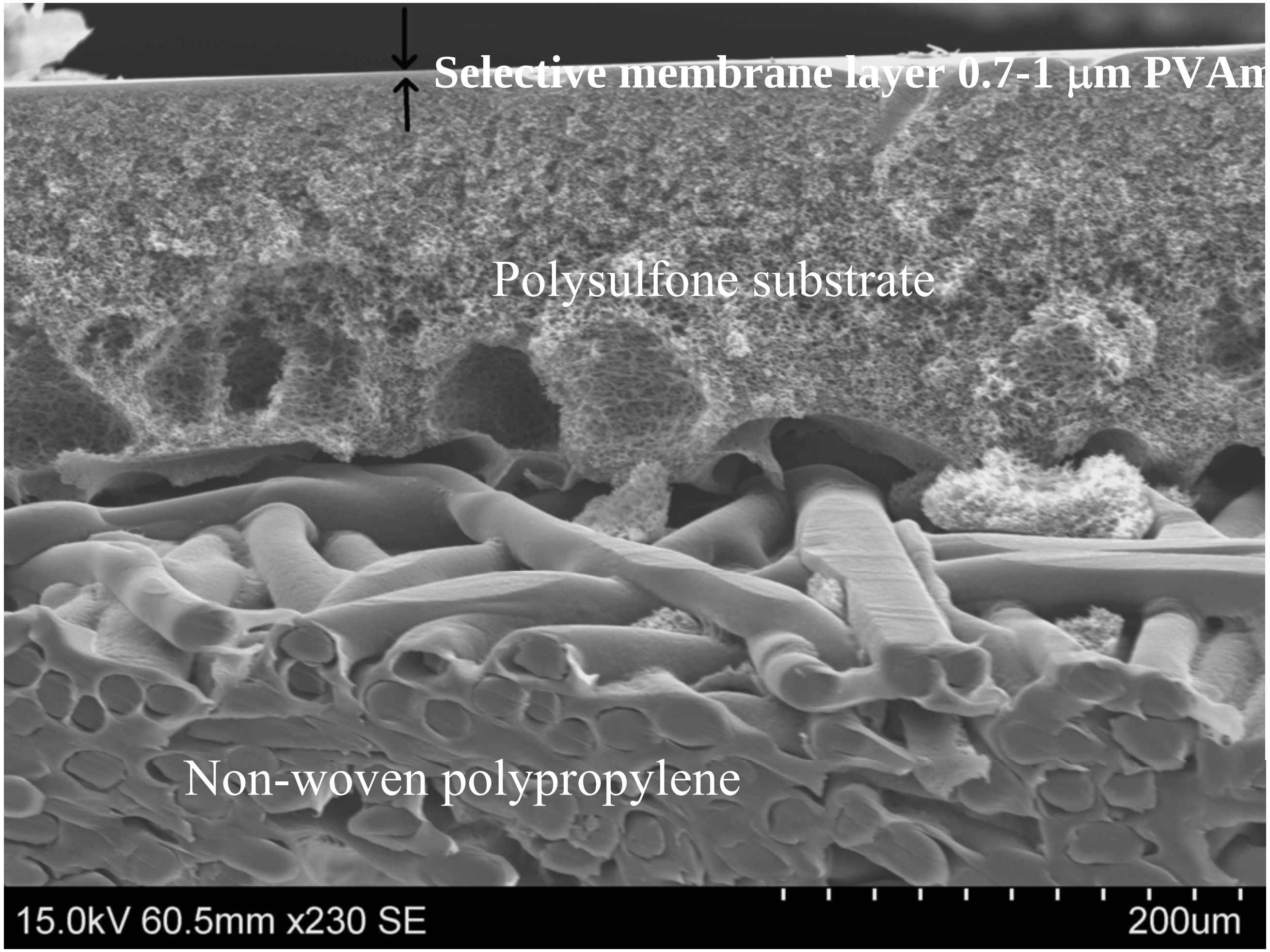
Fickian diffusion

* Facilitated transport of CO_2 dominates over Fickian diffusion

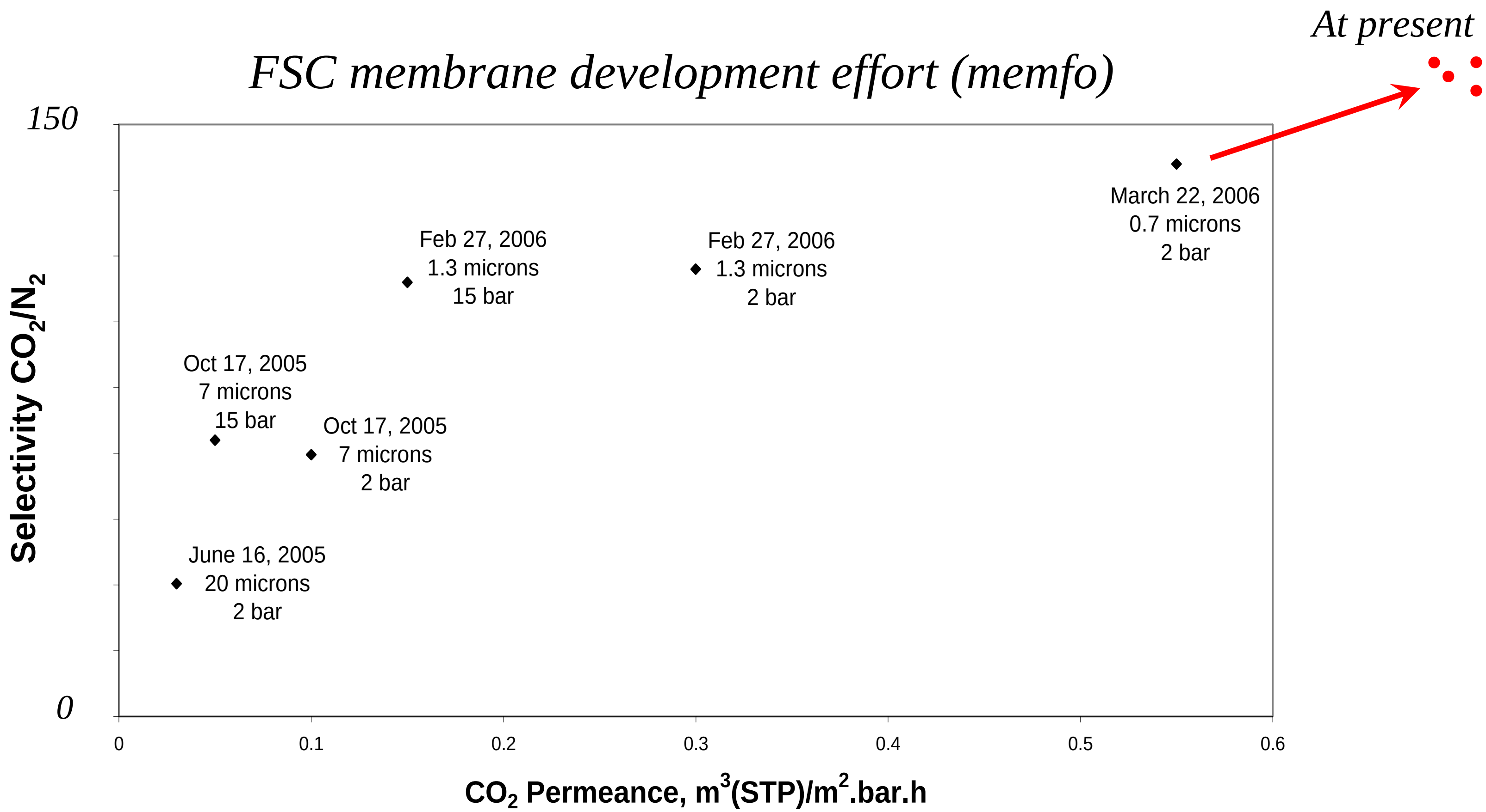
* Membrane needs to be humidified

Kim T-J, et al., J. Polym. Sci. Part B: Polym. Phys. 42 (2004) 426

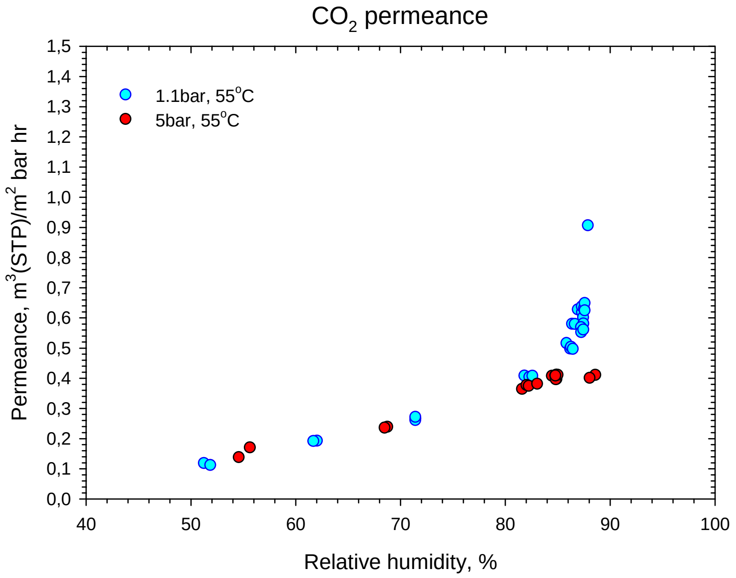
PVAm/PSf FSC membrane

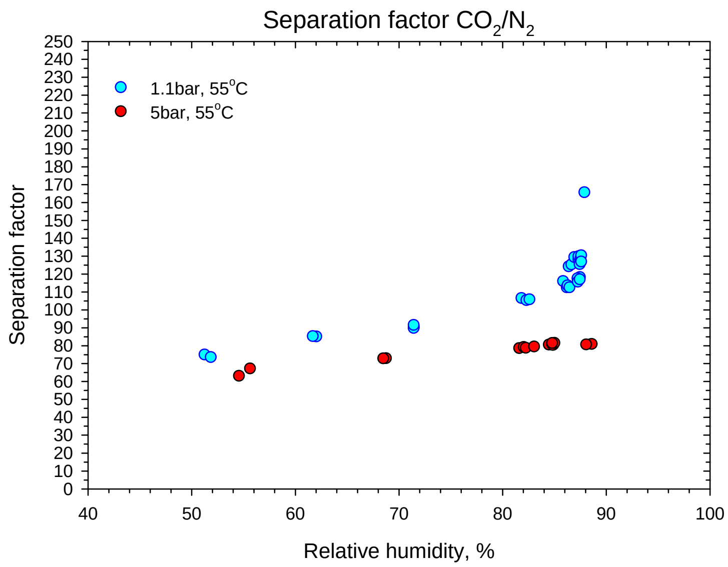


FSC membrane development effort (memfo)

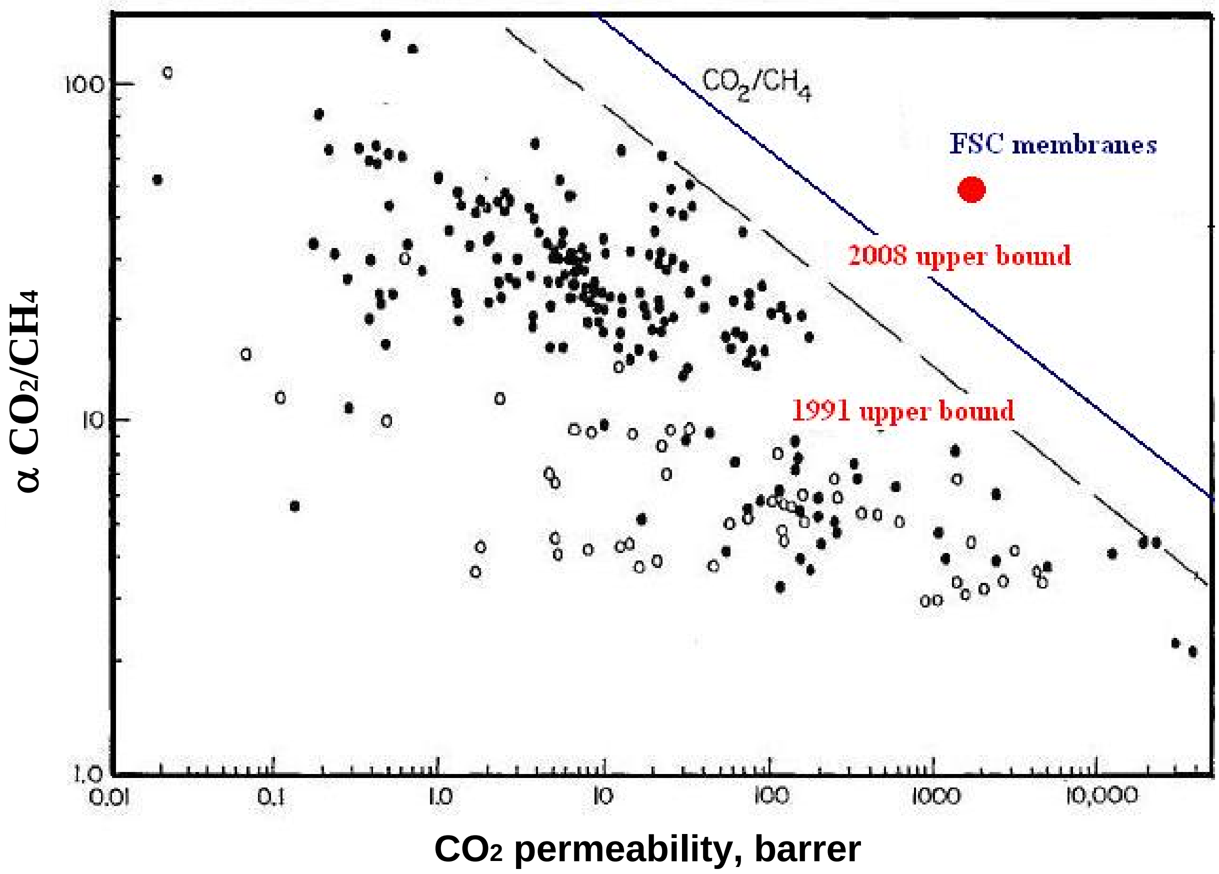


Membrane performance result of sample cuts from large flat sheet membranes prepared by scaled-up method and device
(PVAm membrane, feed gas: 10% CO_2 + 90% N_2)

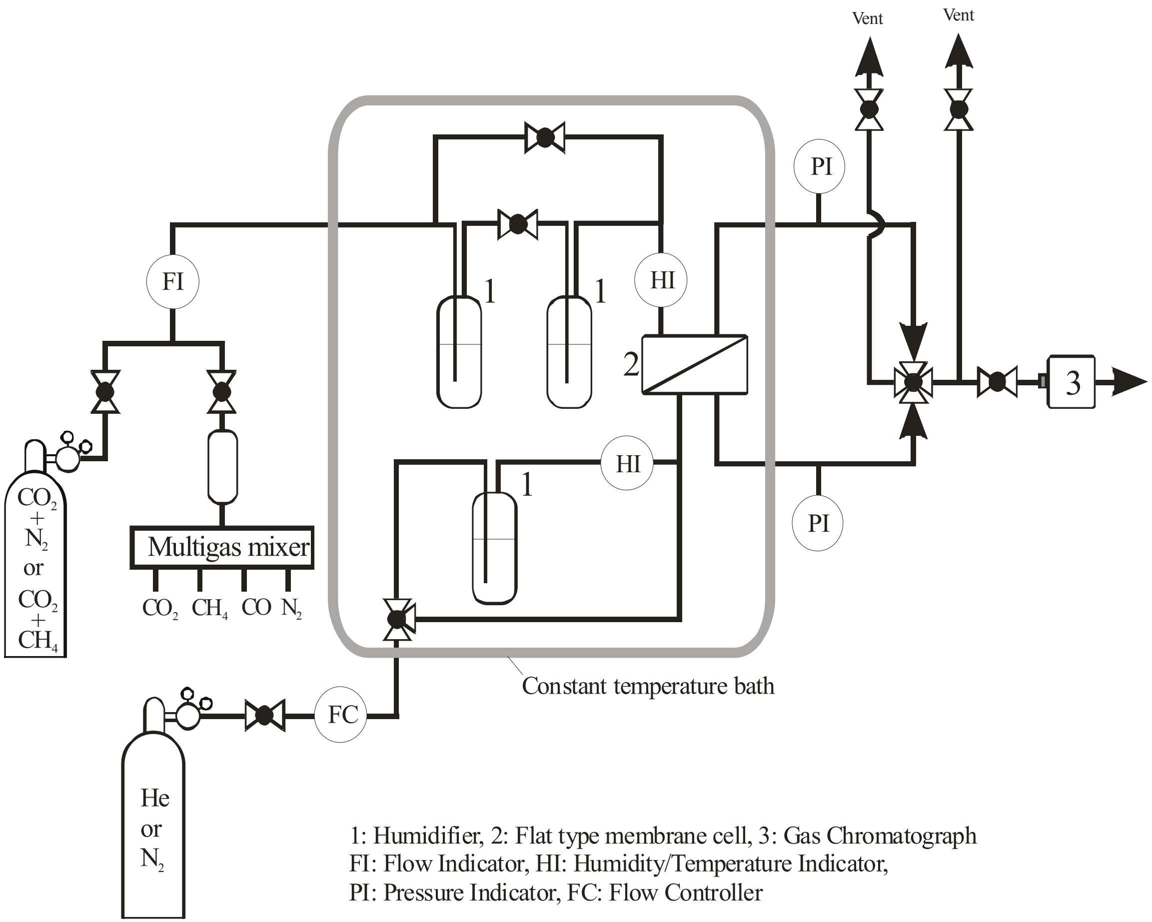




Status of FSC membranes for CO_2/CH_4 separation



Lab-scale experimental setup for CO_2 capture test



1: Humidifier, 2: Flat type membrane cell, 3: Gas Chromatograph
FI: Flow Indicator, HI: Humidity/Temperature Indicator,
PI: Pressure Indicator, FC: Flow Controller

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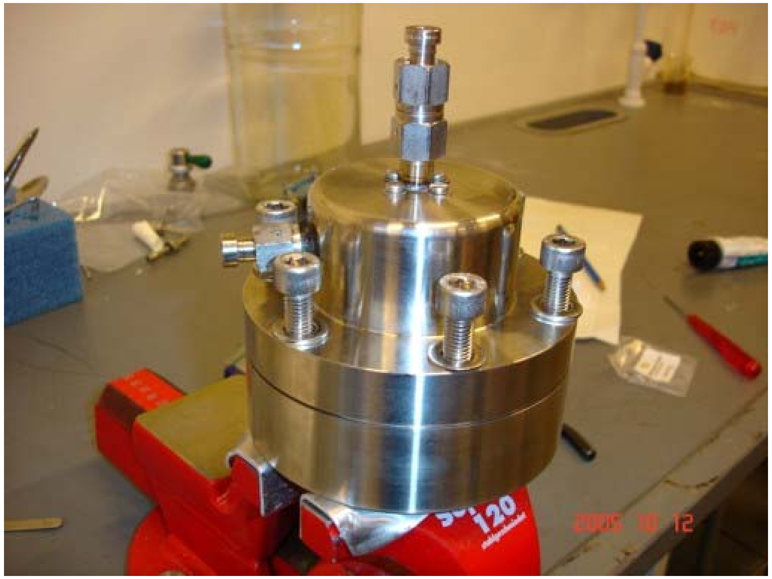
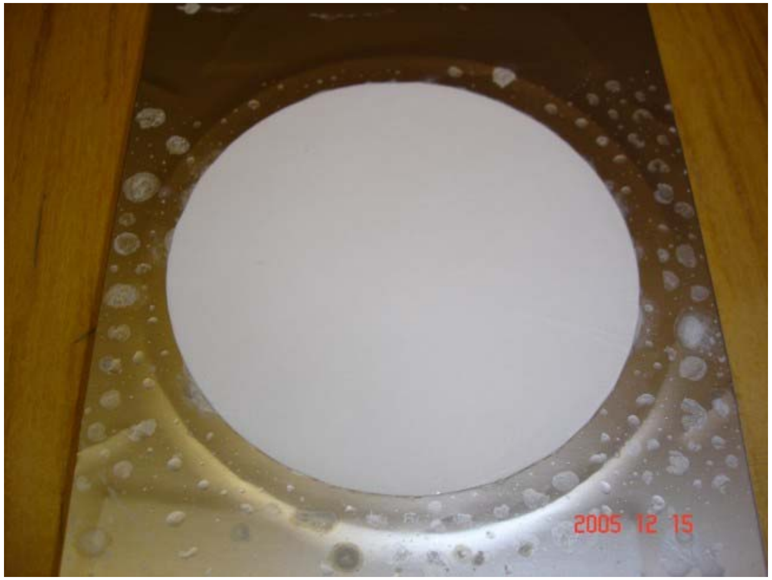
Lab scale FSC membrane preparation and flat sheet membrane test module





Variables of the FSC membrane preparation

- Thickness of PVAm layer on PSf (0.2µm - 50µm)
- Casting-Drying temp/time
- Post heat treatment temp/time or amount & concentration of cross-linking agent
- Source of PVAm (molecular weight, impurities, etc.)
- Physico-chemical properties of support (porosity, hydrophobicity, etc.)
- Support materials (polysulfone, PES, CA, PPO, inorganics, etc.)
- Additives (polymer (PVA), etc.)

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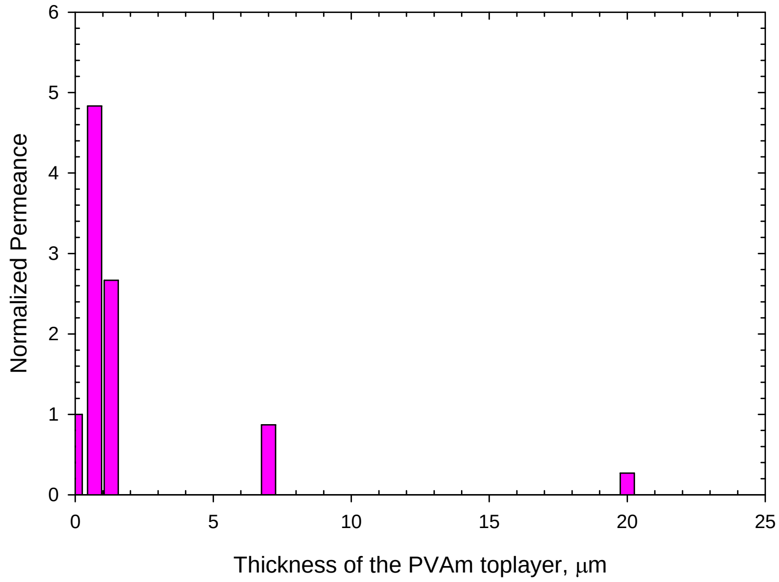
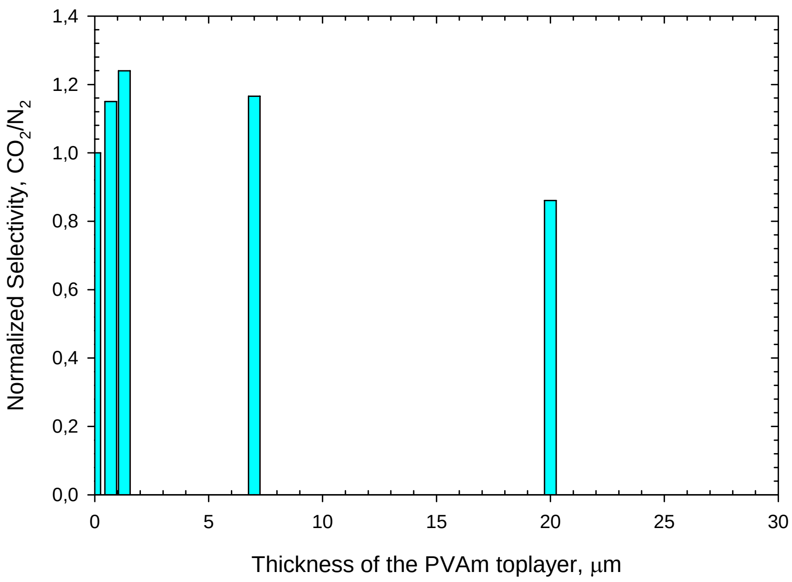
Example) finding of an optimum PVAm layer thickness



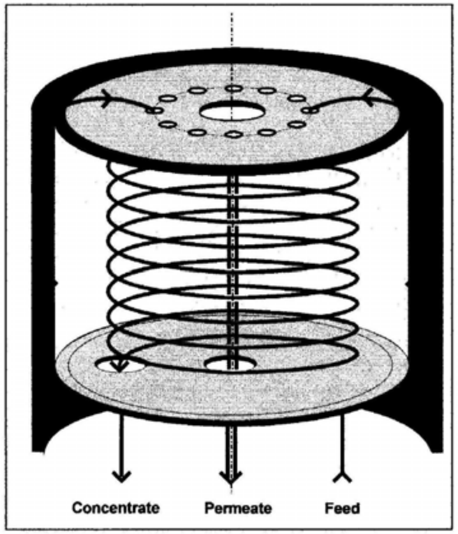


Case 1: up-scaling of flat sheets; ~1 m^2

Module must be able to handle:

- **Potential water condensing without forming a film on the membrane**
- **Testing with both vacuum and sweep on permeate side**
- **Damaged membranes should easily be replaced**
- **Flexible in membrane are (0.5 – 1 m^2)**
- **Optimized flow patterns**

- **None of the commercial modules for gas separation fulfills all these requirements!**
- **→ Plate and Frame seems to be only choice in this phase of up-scaling - such modules are today only used for liquid sep.**



Example:
Schematic figure of the envelope stacked module

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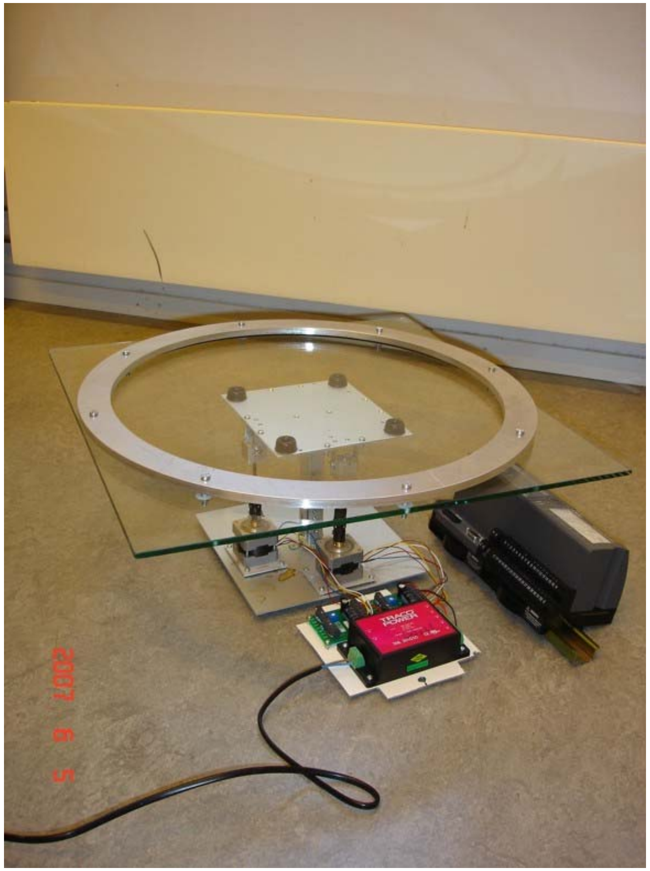
Challenges in up-scaling of membrane preparation

- ✓ Good compatibility of casting solution with support (good film foaming on large area hydrophobic surface)
- ✓ Uniform (& flat) top selective layer of membrane (1micrometer)
- ✓ Uniform post treatment effect on the whole membrane surface
- ✓ Applicability for mass production

Effort to develop pilot scale flat sheet membrane



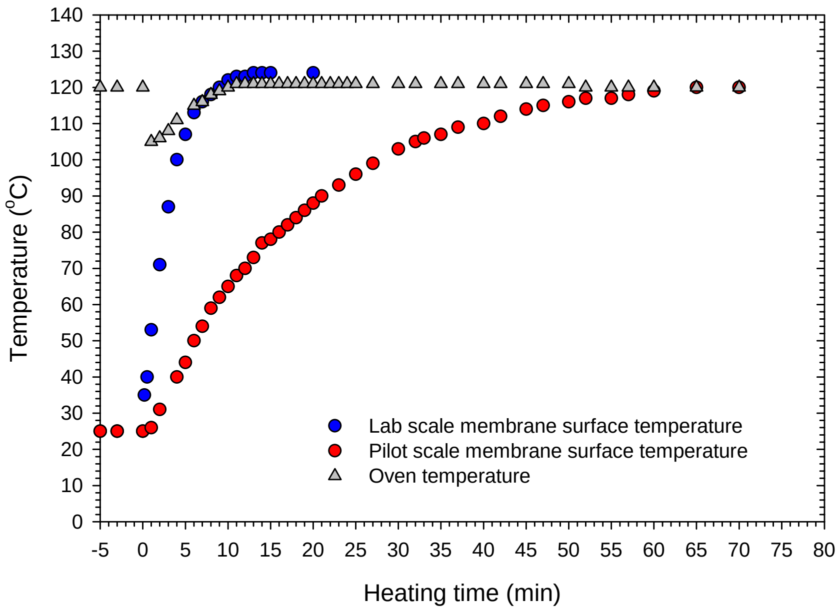
Direct application of lab. scale method ?

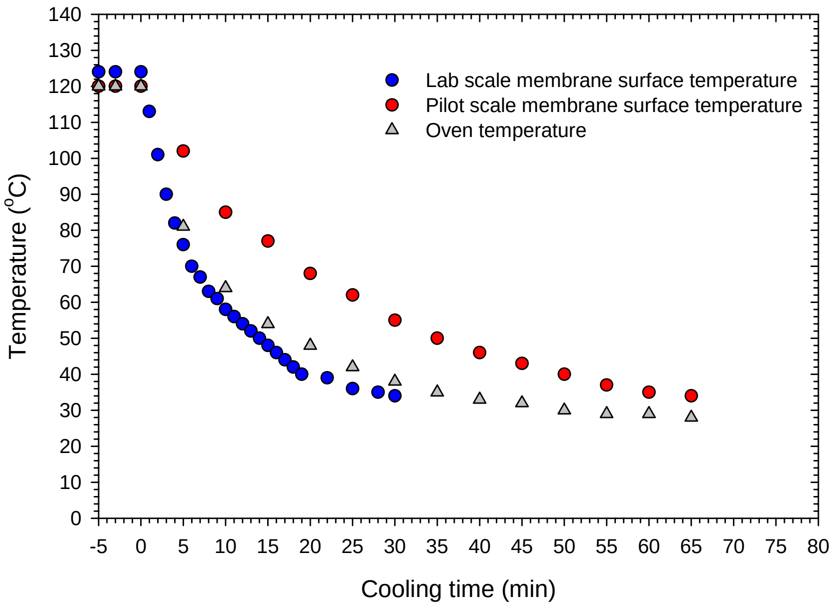
Lab. scale

Diameter 4 – 7cm
Uniform casting of polymer solution
Uniform drying of polymer solution
Uniform thermal & chemical treatment
Easy film forming
Easy handling

Wrinkles and deformation
Bad film forming
Non uniform coating of surface
Different thermal treatment effect

Example) Difference in heat treatment effect between lab and pilot scale devices (surface temperature of membrane during heat treatment & cooling)





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Example) Difference in some physical properties of membrane materials

	Tg °C	Tm °C	Coefficient of linear thermal expansion in/in/°F
Polypropylene	-20 (atactic) 0 (isotactic)	~ 160	1.2×10^{-4}
Polysulfone	185	~ 188	3.1×10^{-5}
Polyvinylamine	-	200-250 (decomposition)	-
Polyvinylalcohol	85	~ 230 (decomposition)	-

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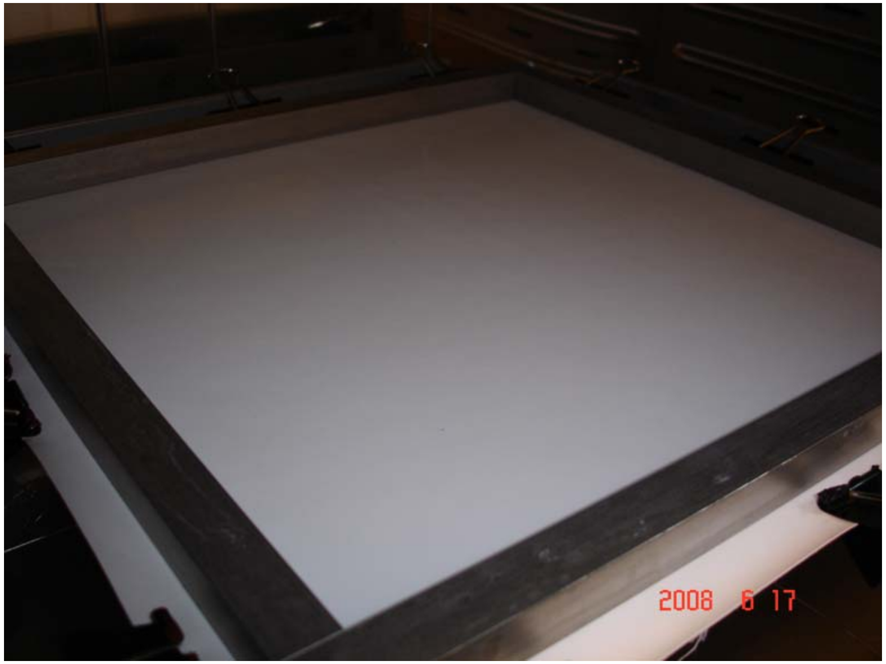
Success!

✓ No wrinkles and no deformation
✓ Good film forming
✓ Large but uniform coating (30cm x 30cm x 1micrometer)



✓Newly devised equipments

*** Holding method of support (equal tension across support)**

*** Support flatness ensured during coating**

✓Membrane preparation parameters adjusted

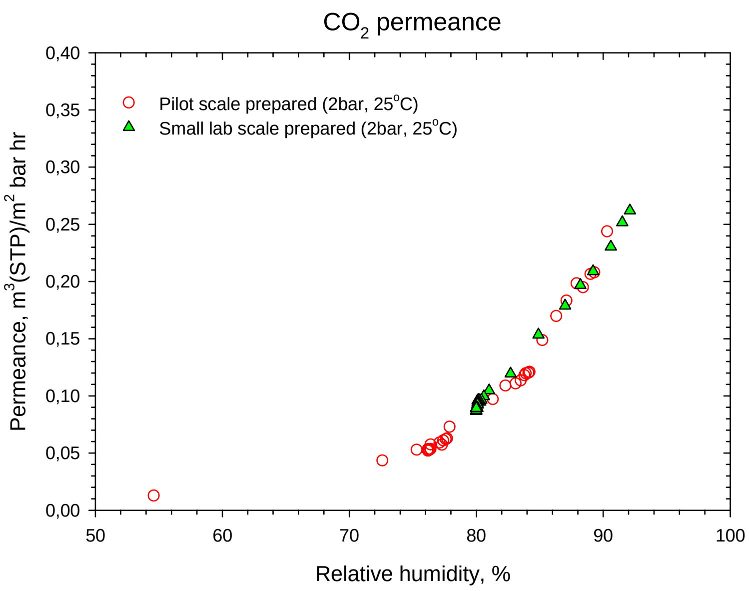
*** Change of solvent**

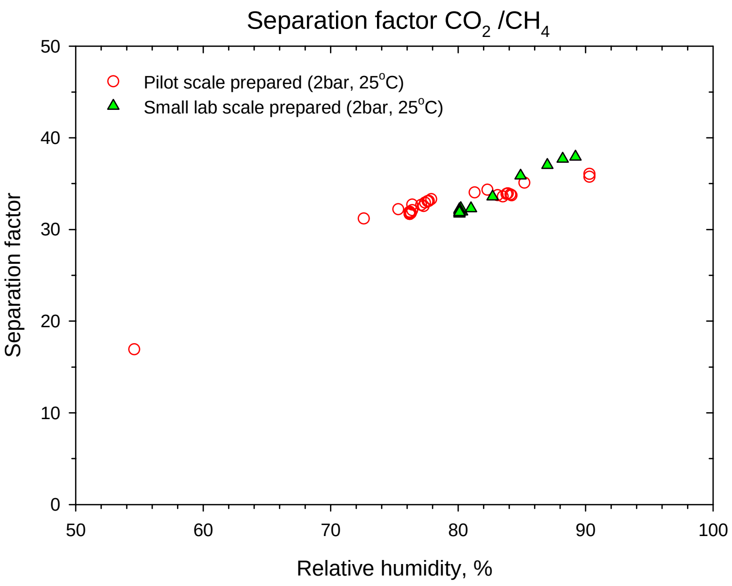
*** Change of conc. of cast solution**

*** Change of treatment temperature**

*** Change of treatment time**

Comparison of membrane performance of sample cuts from large flat sheet membranes prepared by scaled-up method and device with lab-scale prepared membranes (PVAm membrane, feed gas: 10% CO_2 + 90% CH_4)





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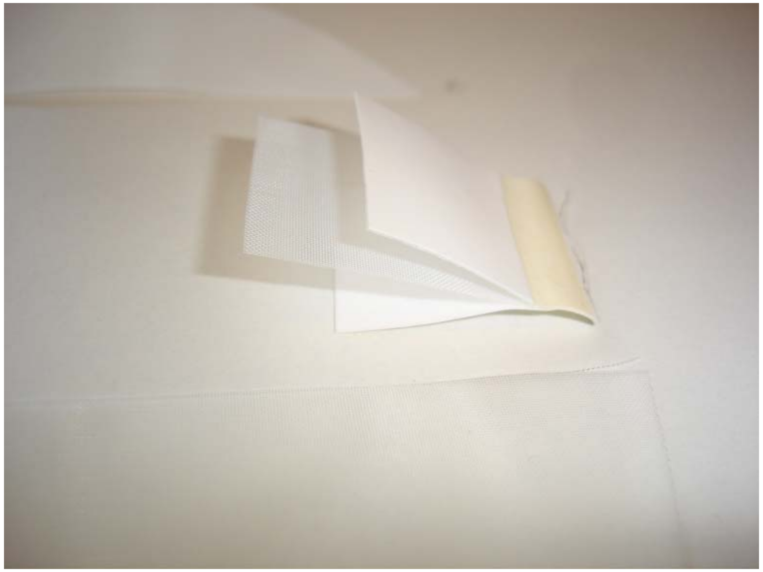
Module development: envelope preparation

Check points

- **- leak tight joint**
- **- mechanical properties change (brittleness, etc.)**
- **- thermoplasticity of non-woven fabric**
- **- thermoproperties of spacer & membrane**

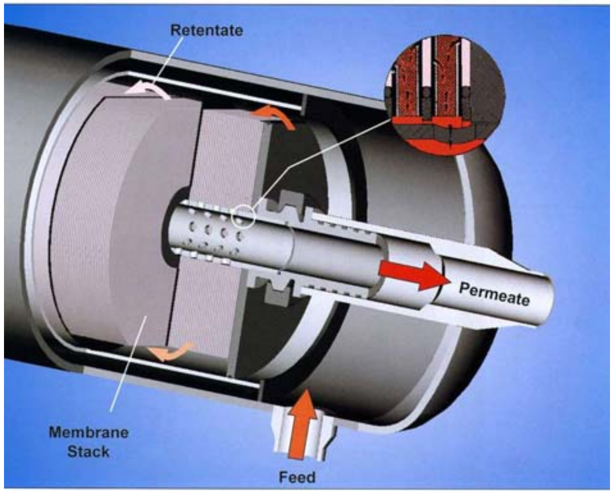


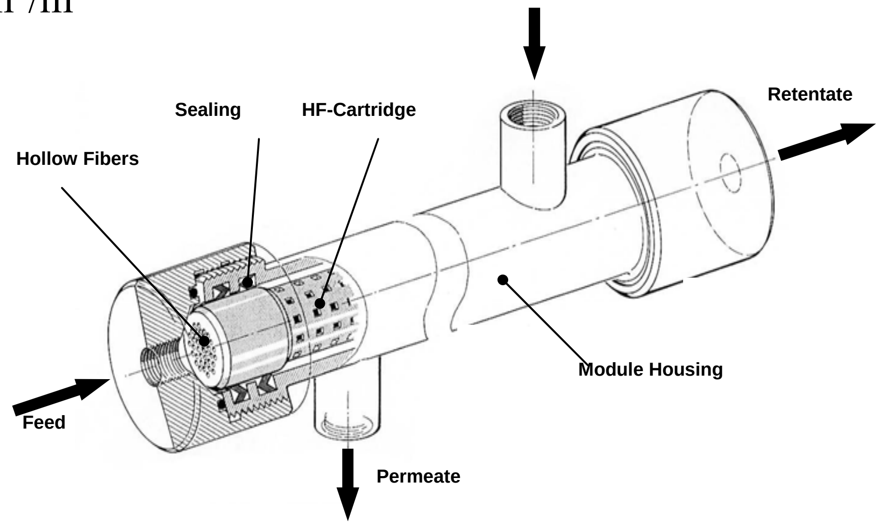
Selection of welding parameters

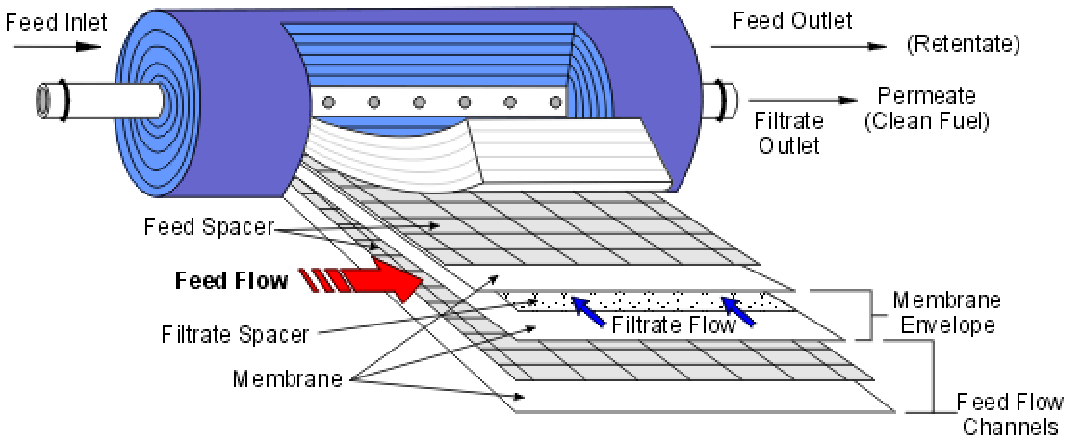
- **- temperature**
- **- pressure**
- **- time**
- **- environment (gas)**

Module: Flat Sheets or Hollow Fibres?

Envelope type: Packing density: 100 – 400 m^2/m^3



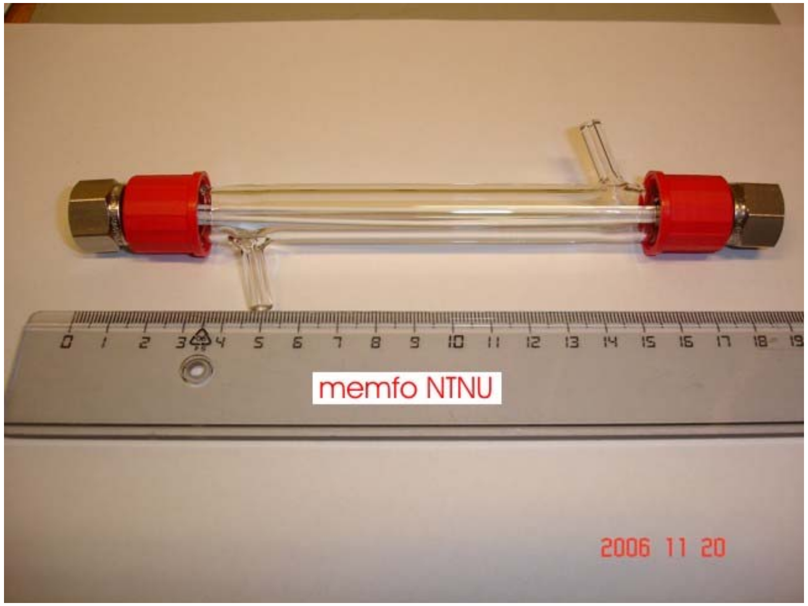




Spiral wound type: Packing density: 300 – 1000m^2/m^3

Hollow fiber:
Packing density:→ 30 000 m^2/m^3

Lab-scale hollow fiber development effort



Preparation of lab. scale hollow fiber module (glass) with commercial PSf fiber

- uniform coating (dip coating)
- contraction & curling of fibers by heat-treatment
- condensing of excessive water
- contact between fibers

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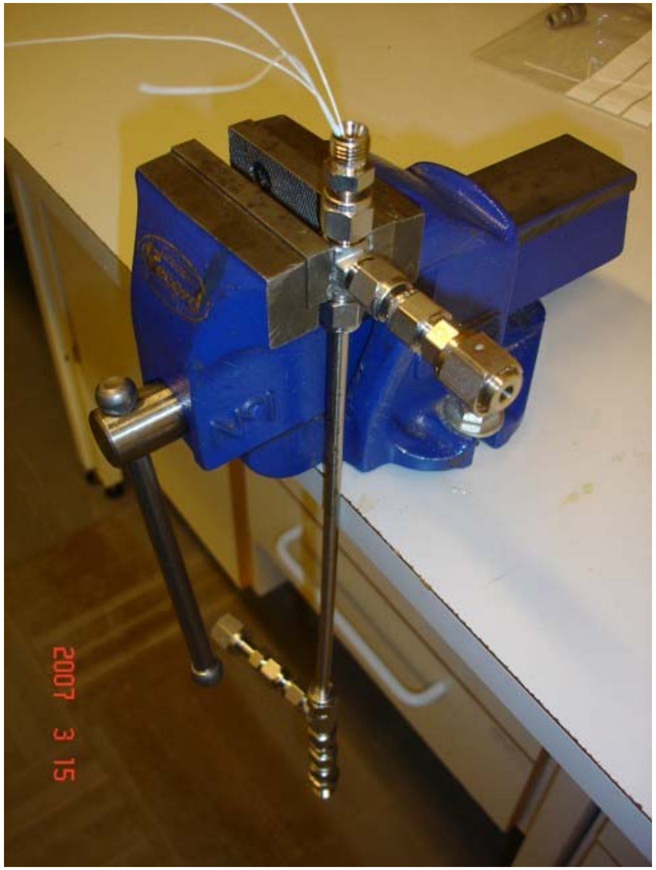
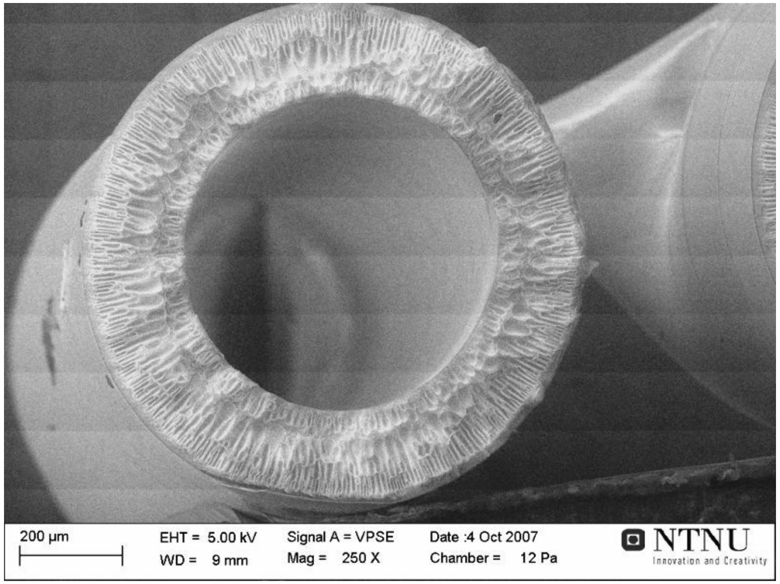
Preparation of lab. scale hollow fibre module (stainless steel)



Case 2: up-scaling of hollow fibers: (time consuming process - at least 5 steps to scale up)

Challenges when preparing the hollow fibres →

- Secure an asymmetric structure porous enough to give less resistance, but sufficiently dense to be able to coat the outer (or inner) surface
- Drying procedures to avoid collapse of the fiber
- Mechanical properties (flexible but robust against pressure)



Hollow fibers from PSf with DO/DI = 1/0.6 mm are now successfully being spun as support

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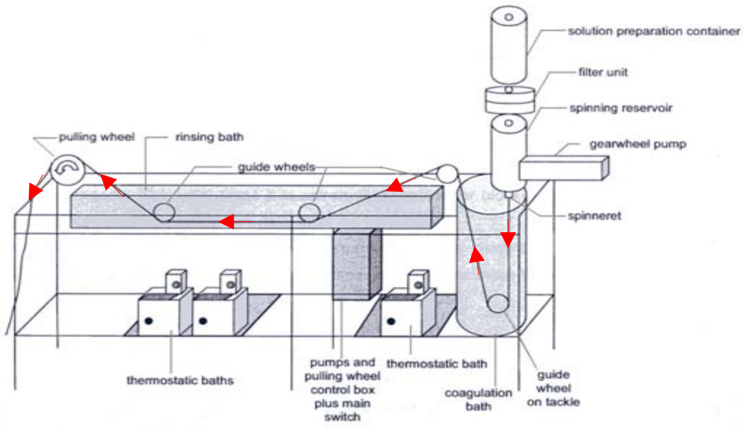
1st step: Spinning the PSf support fibre with optimized properties



Dry-wet spinning technique is employed – possibility if spinning 1200 meters from 1 batch

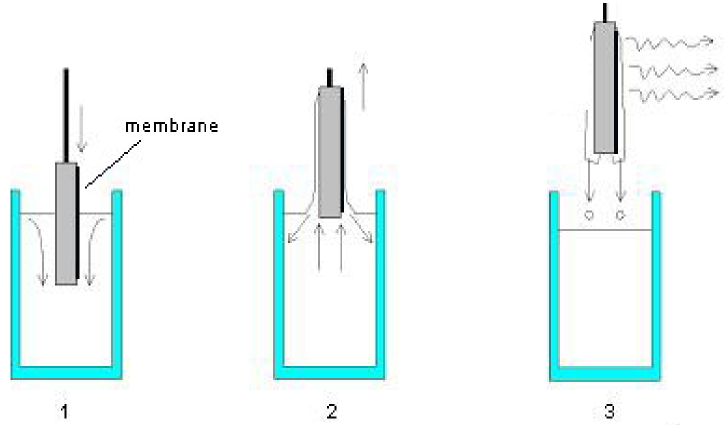
2nd step: Drying of the support fibers

- **Put in bath with glycol to avoid collapse of fiber**
- **Cutting in suitable length**
- **Drying in cabinet; avoid curling**
- **Store them hanging**

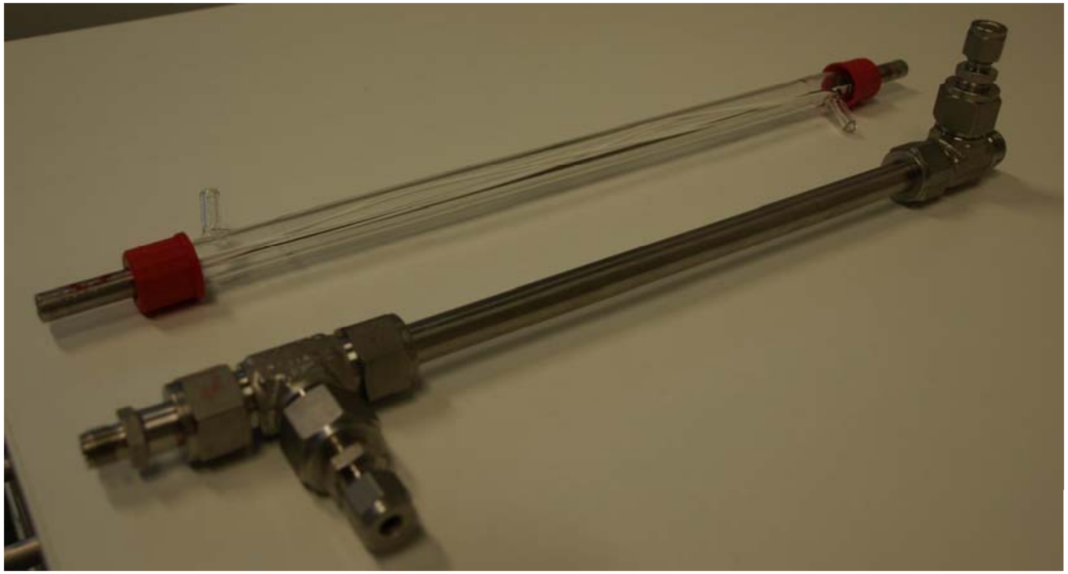
<u>3rd step:</u> Coating with uniform thickness & Heat treatment

- Dip-coating or spray coating?
- The gravity works against you!
- Viscosity of your polymeric solution is hence a very important factor, therefore also the molecular weight of the polymer (here PVAm)

→ ***Automatic dip-coating ?***

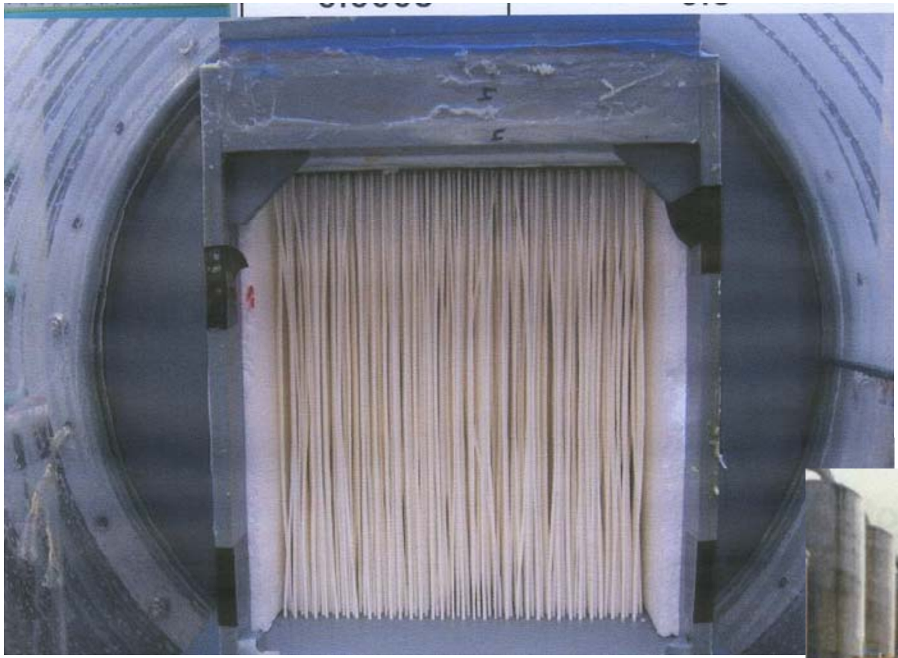


4th step: Mounting in a small module to test separation properties



- About 10 fibres in a glass or steel module to measure separation properties

5th step: Final pilot module



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Durability

✓ FSC membranes for flue gas CO_2 capture

: currently being tested in real flue gas stream at a coal fired power plant

- SO_2
- particles & ashes

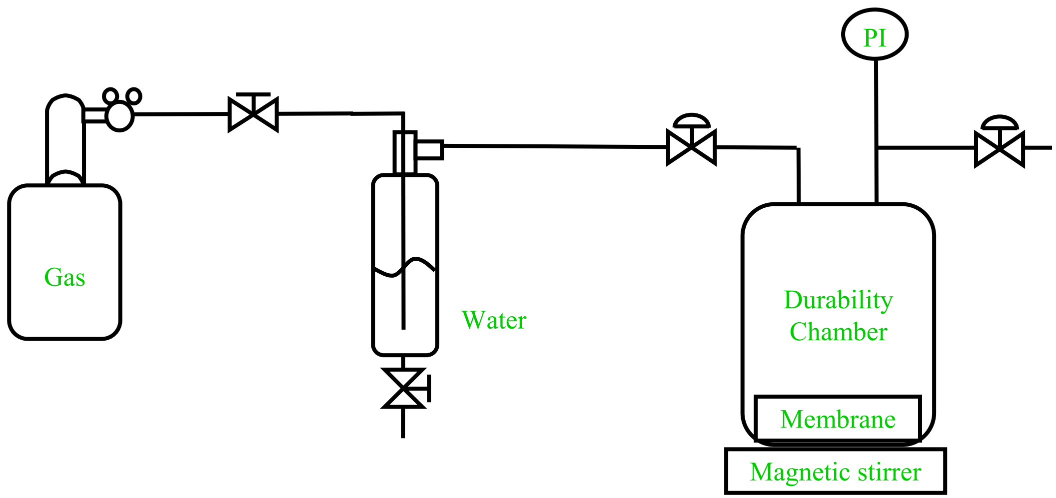
(stable performance against synthetic “pure” flue gas for several months)

✓ FSC membranes for natural gas sweetening: lab scale contamination test is on going

- higher hydrocarbons
- H_2S
- high pressure (70 – 100bar)

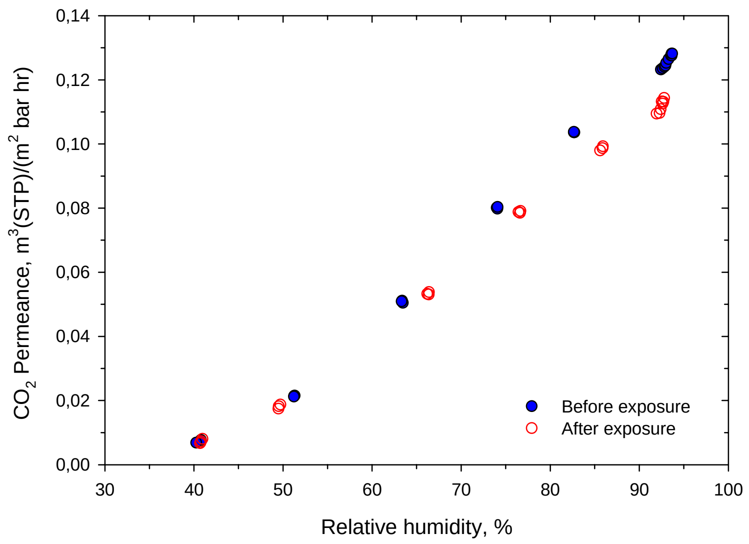
(stable performance against synthetic “pure” natural gas for several months)

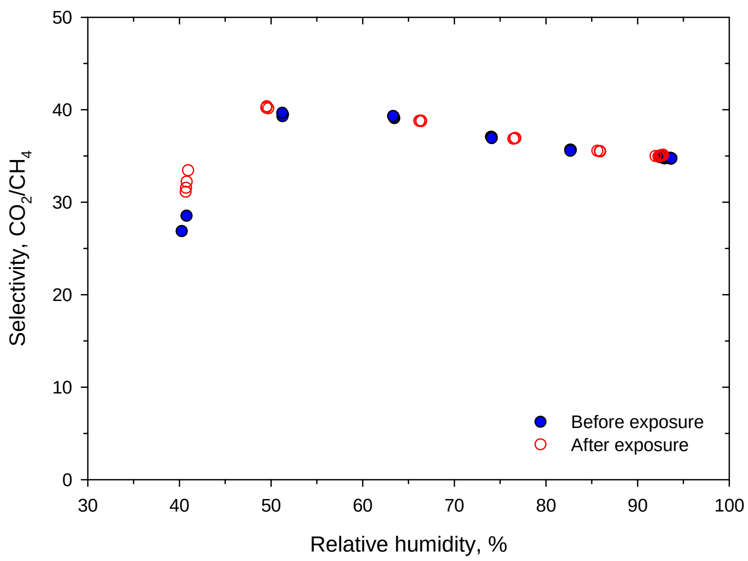
Lab scale experimental setup for durability test



- Exposure to wet Synthetic Gas (84.9% CH_4, 10% CO_2, 4% C_3H_8, 1% H_2S, 0.1% *n*-Hexane)

Comparison of performance of FSC membranes before and after exposure to the synthetic natural gas with an excessive content of H_2S
(PVAm/PVA membrane, feed gas: 10% CO_2 + 90% CH_4)





Potential industrial applications of FSC membranes

1. Post combustion-flue gas (natural gas fired plant, coal fired plant)

Challenges:

- Low partial pressure
- Fly ash, sulfur compounds

2. Natural gas sweetening

Challenges:

- High pressure
- H_2S and higher hydrocarbons

3. Pre-combustion; IGCC

Challenges:

- High temperature

4. Other CO_2-containing gas streams (biogas treatment)

Challenges

- High or wide range CO_2 content
- Various kinds of contaminants

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Comparison with solvent absorption systems

	Membranes	Physical/chemical solvent systems
Energy consumption	Producing sweep gas Pre-treatment (heaters) Compression of feed Recompression of permeate Loss of fuel to permeate	Heating/stripping steam Solvent circulation pumps Loss of fuel to CO_2 stream
Chemical consumption	None	Solvent make-up
Volume and weight	Generally low (10 000-30 000 m^2/m^3)	High
Maturity	Emerging technology	Conventional technology
Environment	Environment friendly	Potentially hazardous solvent used

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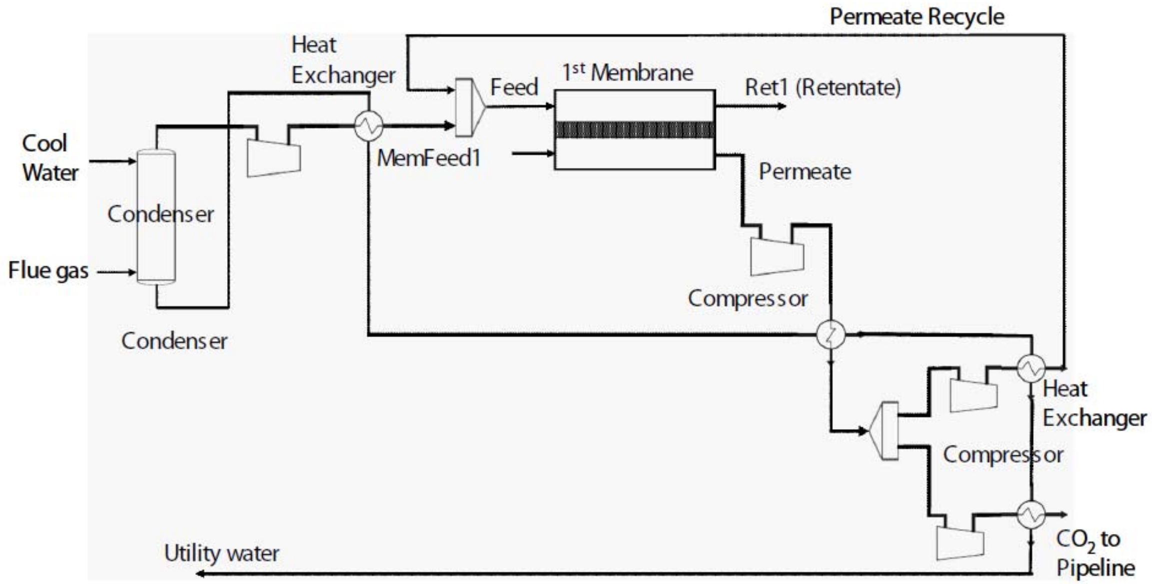
Economic feasibility study through process simulation & optimization

Example) Feasibility study for flue gas CO_2 capture application



Simplified single stage membrane separation process (without sweep flow).

Economic and Process parameters for Gas Processing Cost (GPC)

Total Plant Investment (TPI)	
Membrane module cost, including cost of membrane element (MC)	$5/ft^2
Installed Compressor Cost (CC)	$8650 X (HP/η)^0.82
Fixed Cost (FC)	MC + CC
Base Plant Cost (BPC)	1.12 X FC
Project Contingency (PC)	0.20 X BPC
Total Facilities Investment (TFI)	BPC + PC
Start-up Cost (SC)	0.10 X VOM
TPI	TFI + SC
Annual Variable Operating & Maintenance Cost (VOM)	
Contract & Material maintenance Cost (CMC)	0.05 X TFI
Local Taxes & Insurance (LTI)	0.015 X TFI
Direct Labor Cost(DL) based on 8h/day per 25MMSCFD	$15/h
Labor Overhead Cost (LOC)	1.15XDL
Membrane replacement costs, (MRC)	$3/ft^2 of membrane
Utility Cost, $/kWh, (UC)	0.07/kWh
VOM	CMC + LTI+DL+LOC+MRC+UC
Annual Capital related cost (CRC)	0.2 X TPI
Gas Processing Cost, $/MSCF of flue gas (GPC)	(CRC + VOM) / [365 X OSF X Q_f X (1-SCE) X 1000]
Other assumptions	
On-Stream Facrtor (OSF)	96%
Net Feed flow rate, MMSCFD, (Q_f)	1068 MMSCFD
Stage Cut Equivalent, (net permeate flow rate)/(net feed flow rate), (SCE)	Q_p/Q_f
Membrane life (t)	4 years
Compressor Efficiency (η)	0.8

S.A. Stern et al., J. Membr. Sci. 320 (2008) 108-122

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45% Permeate Recycle
Recovery = 90.03%

Name Stream	Flue Gas	MemFeed1	Feed	Cool Water	Utility Water	Ret1	CO2 to Pipeline
Vapour Fraction	0.996835	1	1	0	0	1	1
Temperature [C]	50	60	59.92	5	32.34	59.92151	34
Pressure [bar]	1	4.050	4	2	1	4	100
Molar Flow [MMSCFD]	1200	1067.78	1184.93	8051.37	8183.59	924.96	142.98
Mass Flow [lb/hr]	3802166	3540582	4087376	15928267	16189852	2873722	667509

Name Stream	Flue Gas	MemFeed1	Feed	Cool Water	Utility Water	Ret1	CO2 to Pipeline
Nitrogen	0.706071	0.7935	0.7228	0.0000	0.0000	0.9041	0.0777
CO2	0.119312	0.1341	0.2099	0.0001	0.0001	0.0155	**0.9015**
Oxygen	4.86E-02	0.0546	0.0513	0.0000	0.0000	0.0599	0.0208
Water	0.126013	0.0178	0.0160	0.9999	0.9999	0.0205	0.0000

	MEM1
Area [m^2]	1.26E+06
Pressure ratio (ψ)	40

E (MJ/kg CO2 captured)	1.98
Gas Processing Cost (GPC)	0.62

Capture cost
~ 38$/ton CO_2
~ 26€ /ton CO_2

On-going………

- Development of larger scale flat sheet membrane
- Development of hollow fiber type membrane
  - Spinning of PSf fiber
  - Coating / Drying / post-treatment technique
- Pilot module test
- Durability test
- Feasibility study & optimal process proposal (process simulation)

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