Energy research Centre of the Netherlands

Hydrothermal stability of a new hybrid membrane in dehydration applications

Jaap Vente

Approach

Four way competences:

- Materials research
- System development
- Process design
- Implementation facilitation

Five different lines of applications

- Pervaporation
- NH_3 separation
- Oxygen production
- Hydrocarbons separations
- Hydrogen purification

Why dehydration with membranes?

By 2015 potential energy savings:

- NL: 7 PJ/yr (2% of industrial energy consumption)
- World: 240 PJ/yr

Production of e.g.

- Esters and resins
- Methyl ethyl ketone (MEK)
- Ethanol
- Ureum
- Acrylic acid

Industrial performance demands

Standard ECN tests: 5 wt.% water in butanol

Fluxes	5 kg/m^{2}h
Selectivity	> 220
Longevity	2 - 3 years

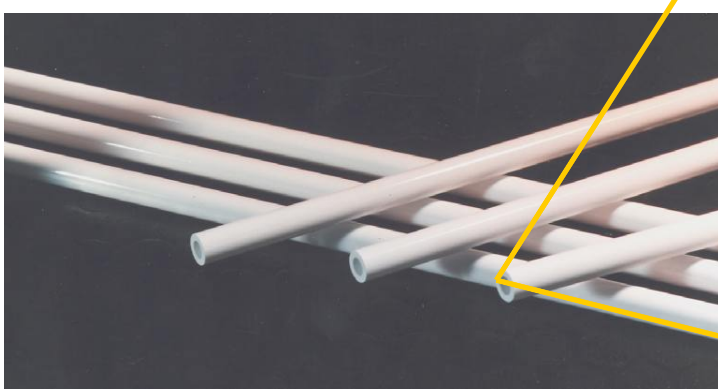
Conditions:

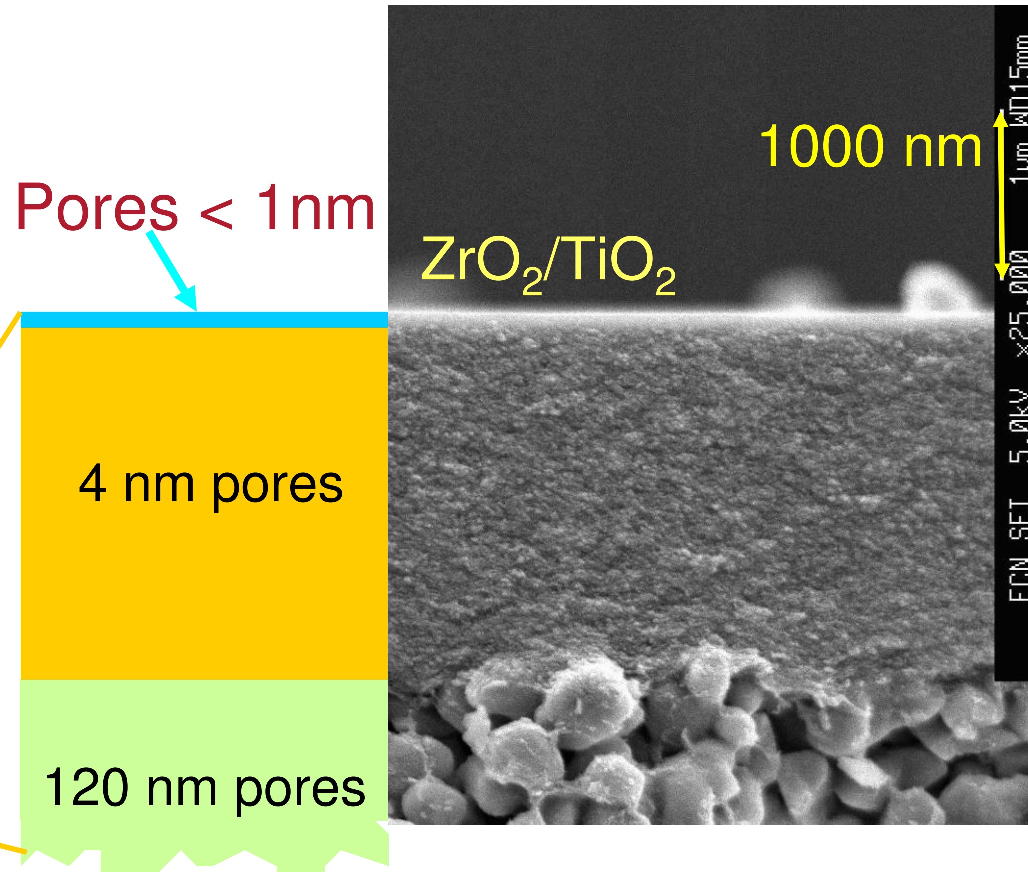
Various pH

Temperatures up to 150℃

ECN

Tubular microporous membranes





Materials covered

Previous developments:

- SiO_2
- Methylated SiO_2

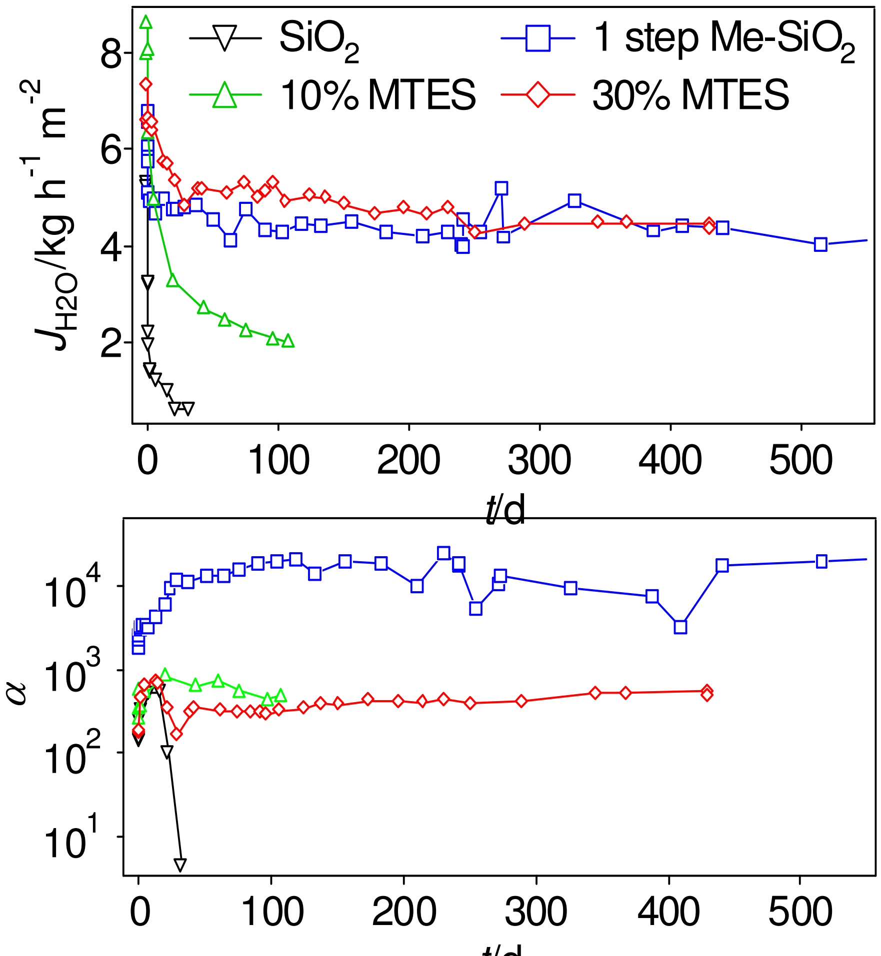
New leads:

- TiO_2
- ZrO_2
- Hybrid silica, organic bridges

(Ceramic supported polymers)

ECN

SiO_2 – Me-SiO_2 pervaporation results (95ºC)



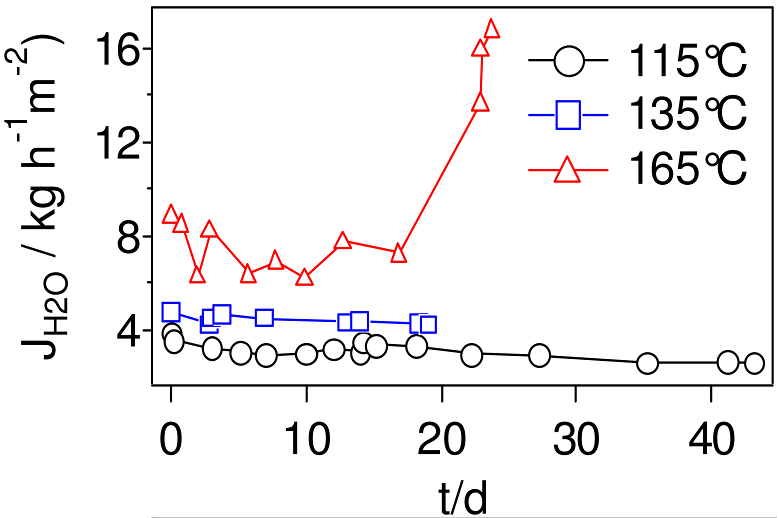
5 wt.% H_2O in BuOH, 10 mbar

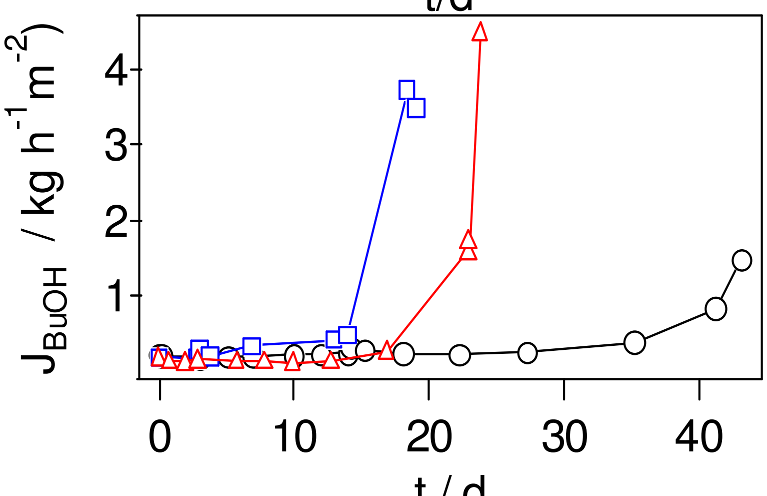
Addition of MTES gives better performance with time

Constant performance possible for over 18 months!

Published data Chem.Comm.2004, 834-835

SiO_2 – Me-SiO_2 pervaporation up to 165ºC





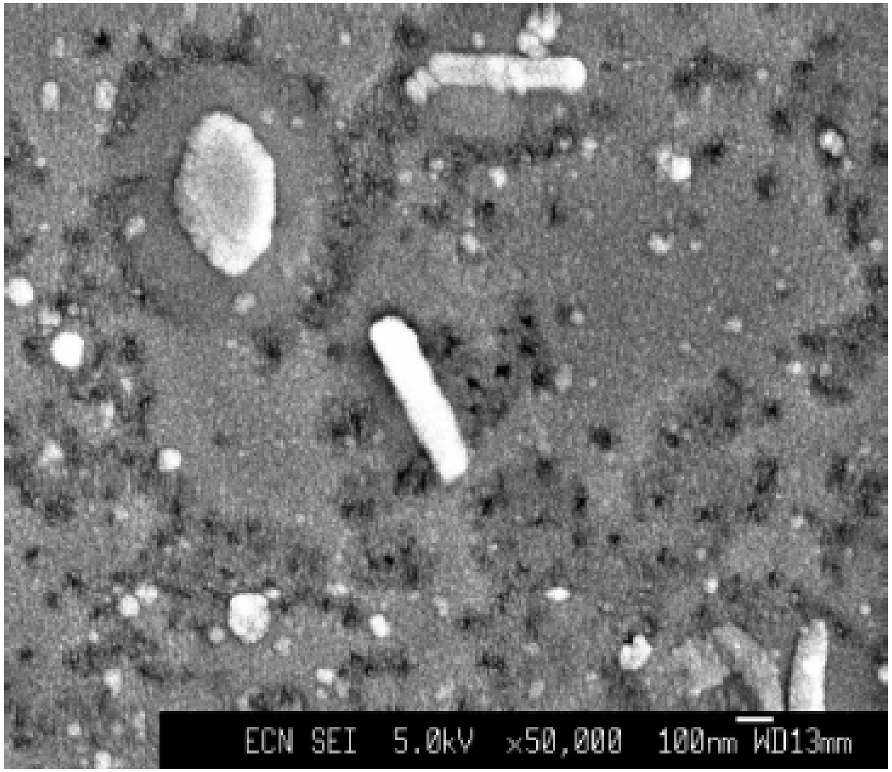
- single step Me-SiO_2
- 2.5 wt.% H_2O in BuOH, 10 mbar
- Failure within weeks
- No clear relation with temperature

Membrane surface after testing (Me-SiO_2)

Severely damaged

Dense white particles

Many pinholes



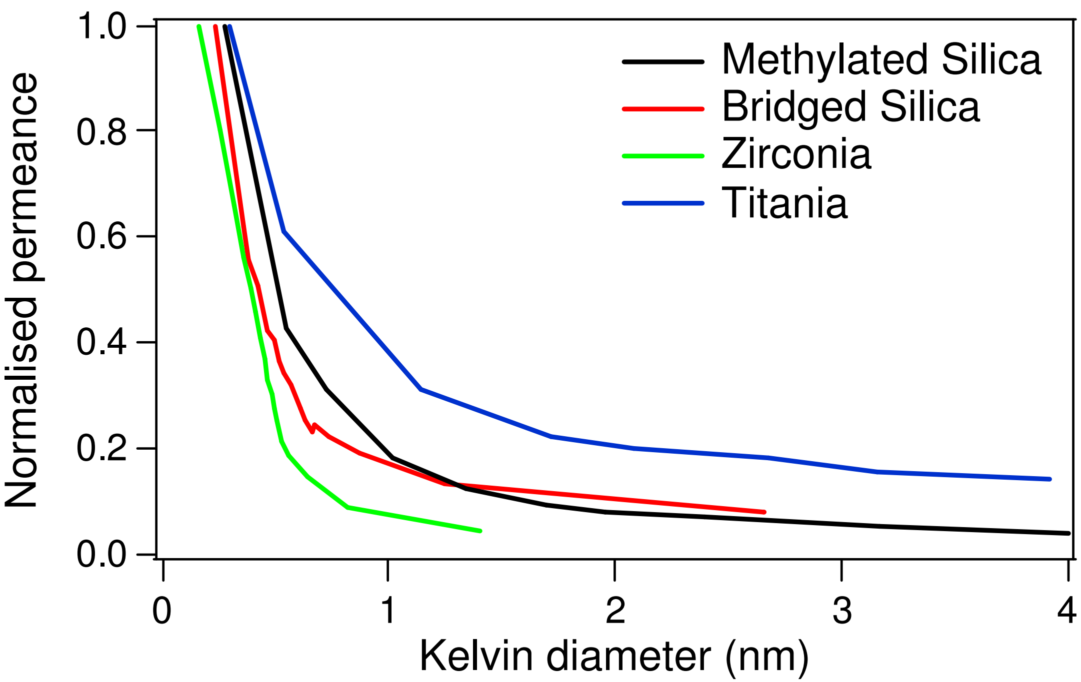
Illustrative example
(Me-SiO_2, 135°C, 7 days)

Pore size distribution new membranes

Permporometry with H_2O

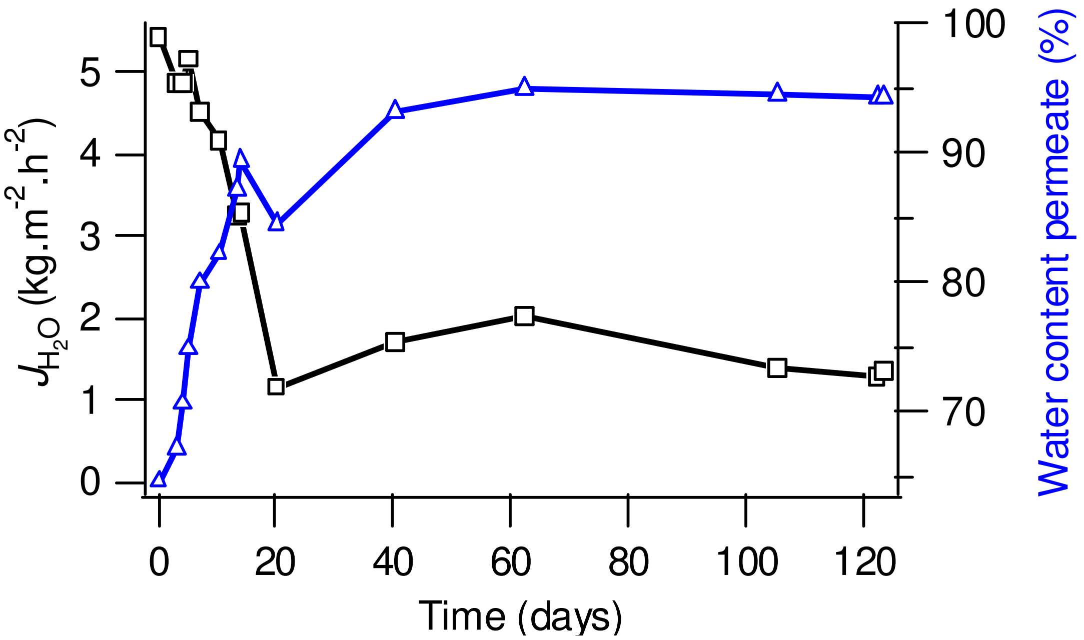
Suitable for thin toplayers

All membranes similar



N_2 and mercury adsorption methods are for bulk material, not for thin layers!

Pervaporation with zirconia membrane



95℃, n-butanol/H_2O (95/5%)

Flux decline, but stable after 20 days

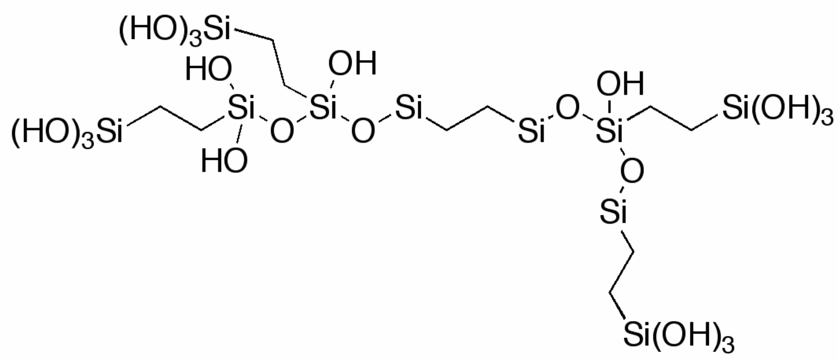
Operating for at least 120 days

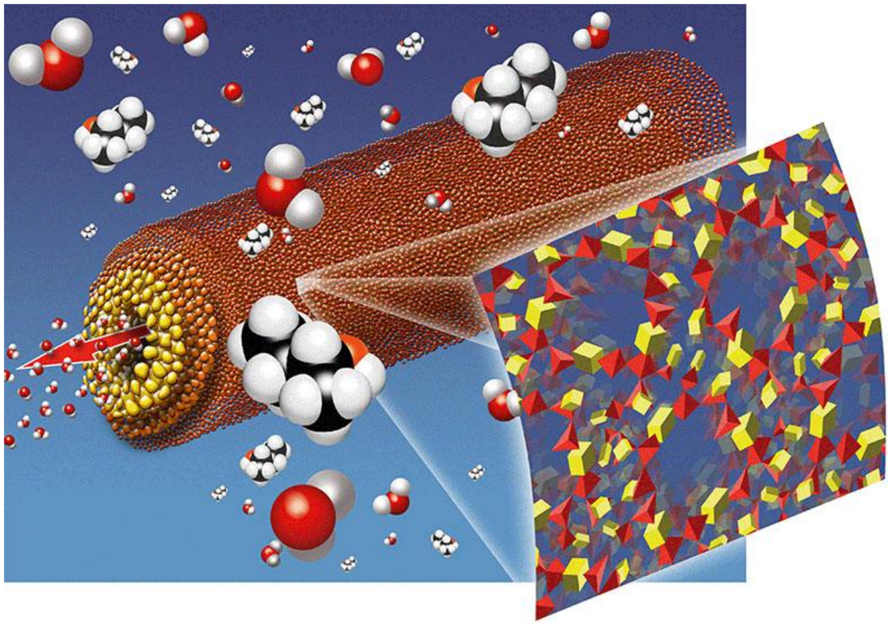
Hybrid membranes from bisfunctional silica precursors

replacing Si—O—Si bonds by Si—C—C—Si bonds

$(OC_2H_5)_3 - Si - CH_2 - CH_2 - Si - (OC_2H_5)_3$

(bis(triethoxysilyl)ethane, BTESE)

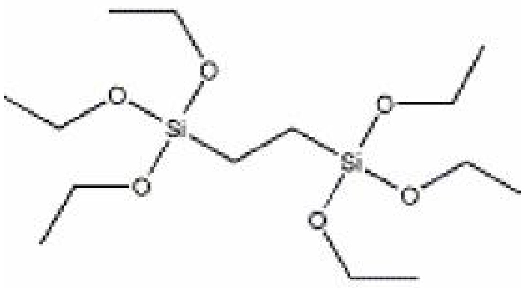




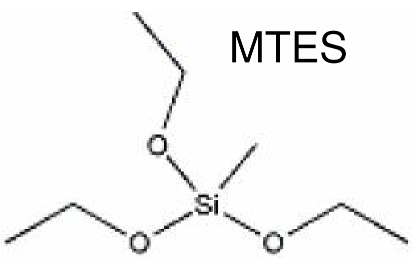
Patented in collaboration with Univ. of Twente and Univ. of Amsterdam (Ashima Sah, Andre ten Elshof, Hessel Castricum, Marjo Mittelmeijer)

New membrane materials: Hybrid membranes

BTESE



MTES



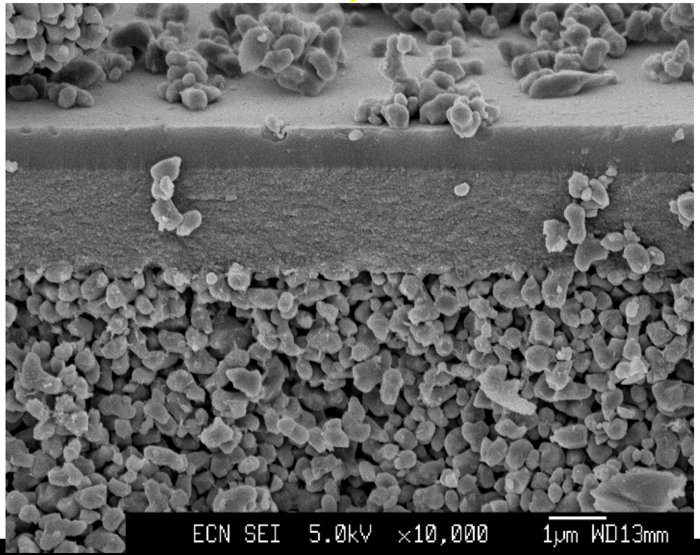
Mix in EtOH

Water, HNO_3 , EtOH

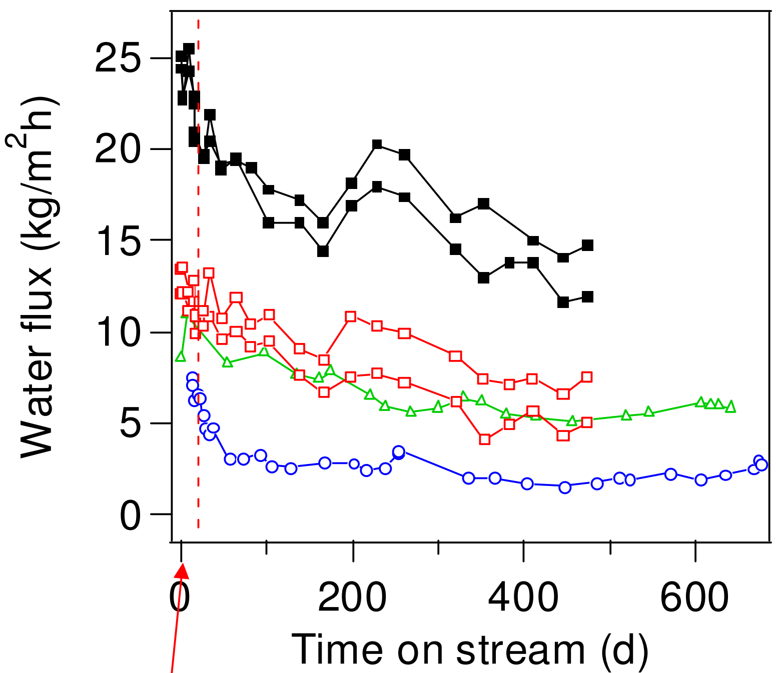
Mix

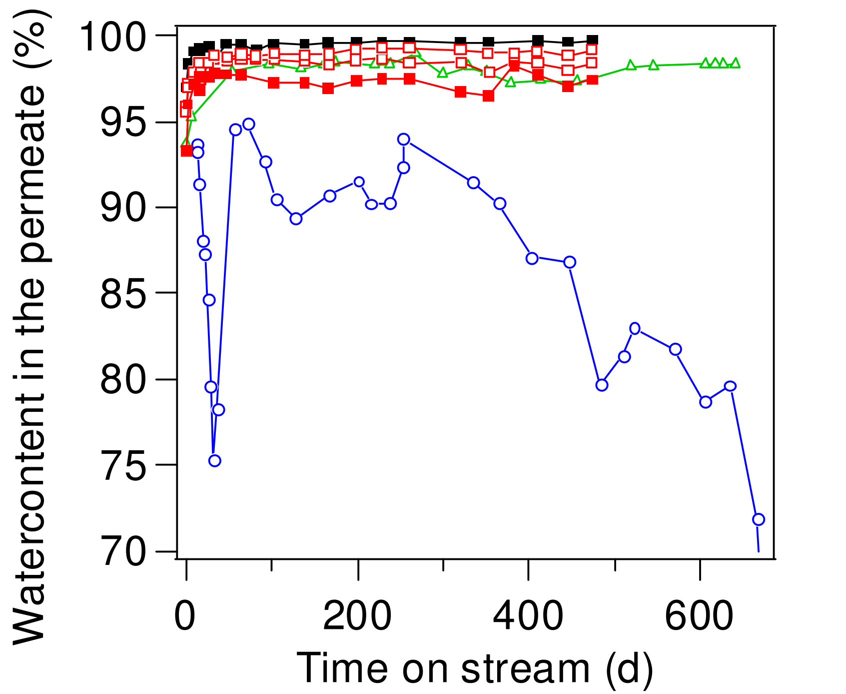
Reflux at 60ºC, 3 hrs

Coating and calcination



Performance hybrid membranes (1) (150ºC)



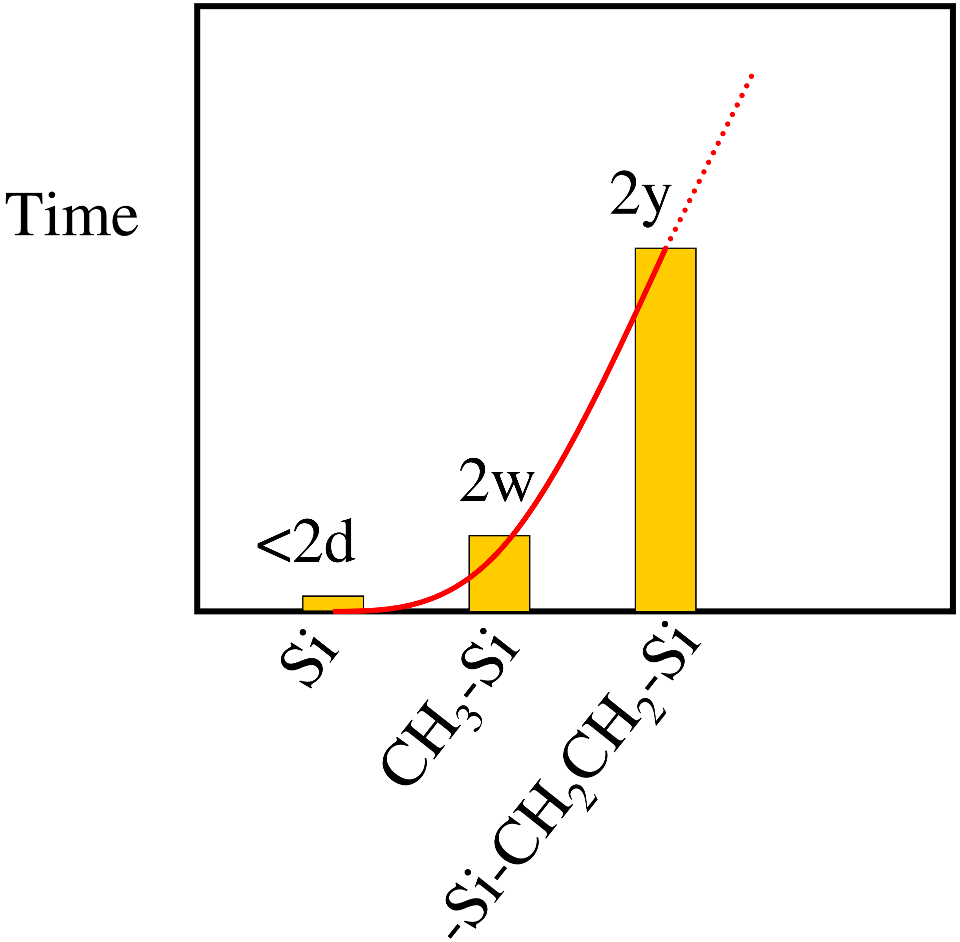


Me-SiO_2 stability

Feed: 5% H_2O in BuOH

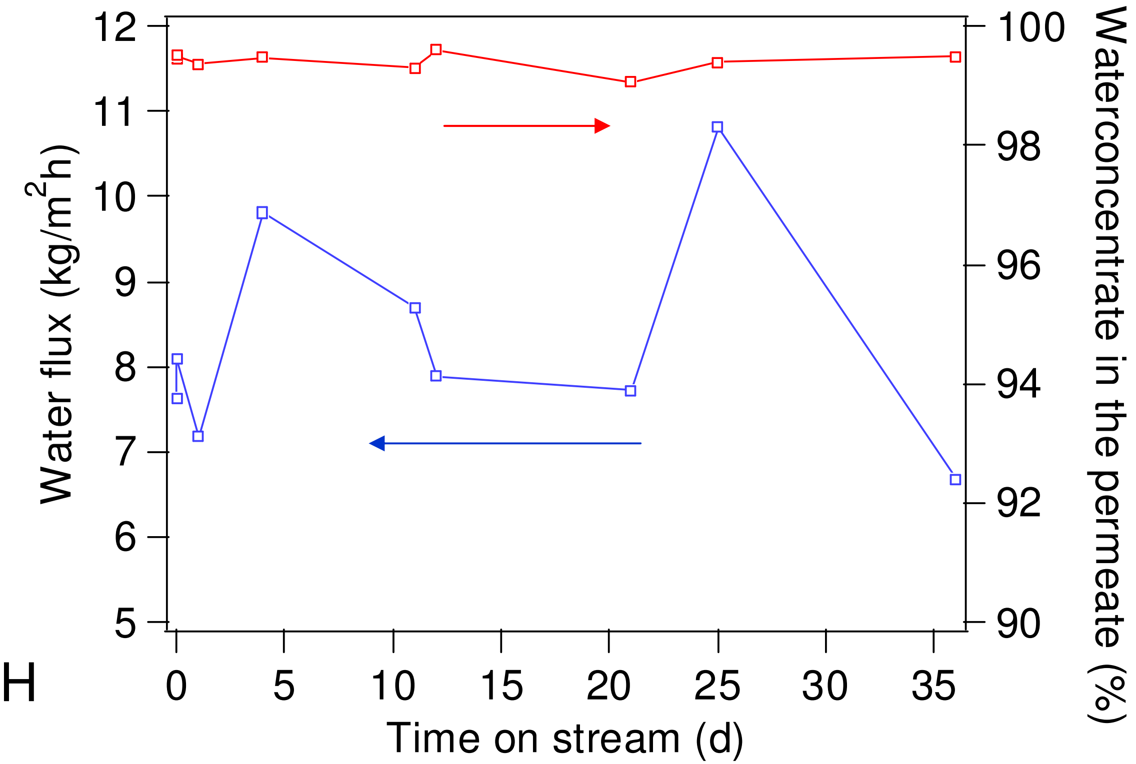
T = 150 C

Hydrothermal stability at 150ºC



ECN

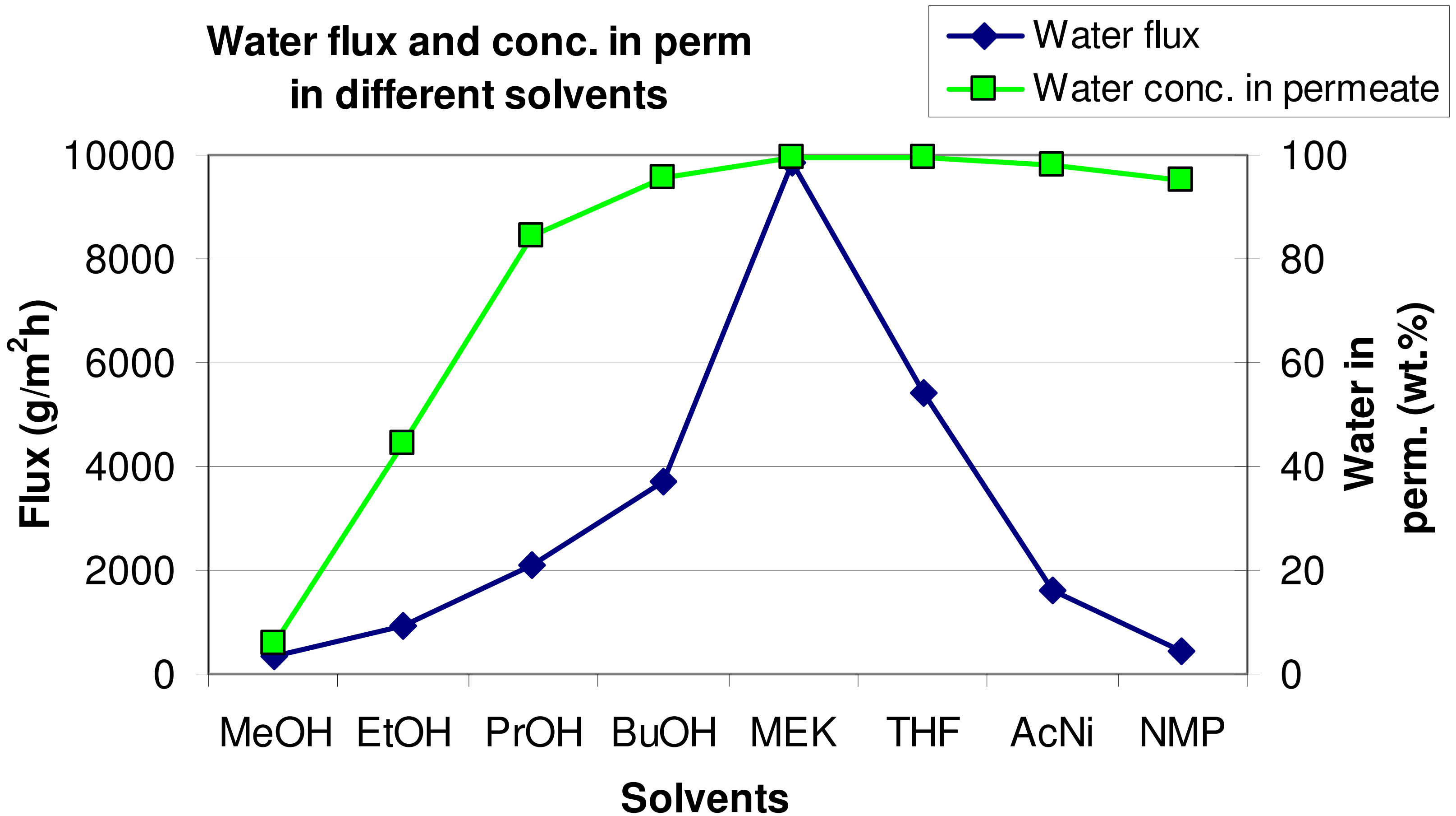
Performance hybrid membranes (2) (190ºC)



Feed: 2,5% H_2O in BuOH

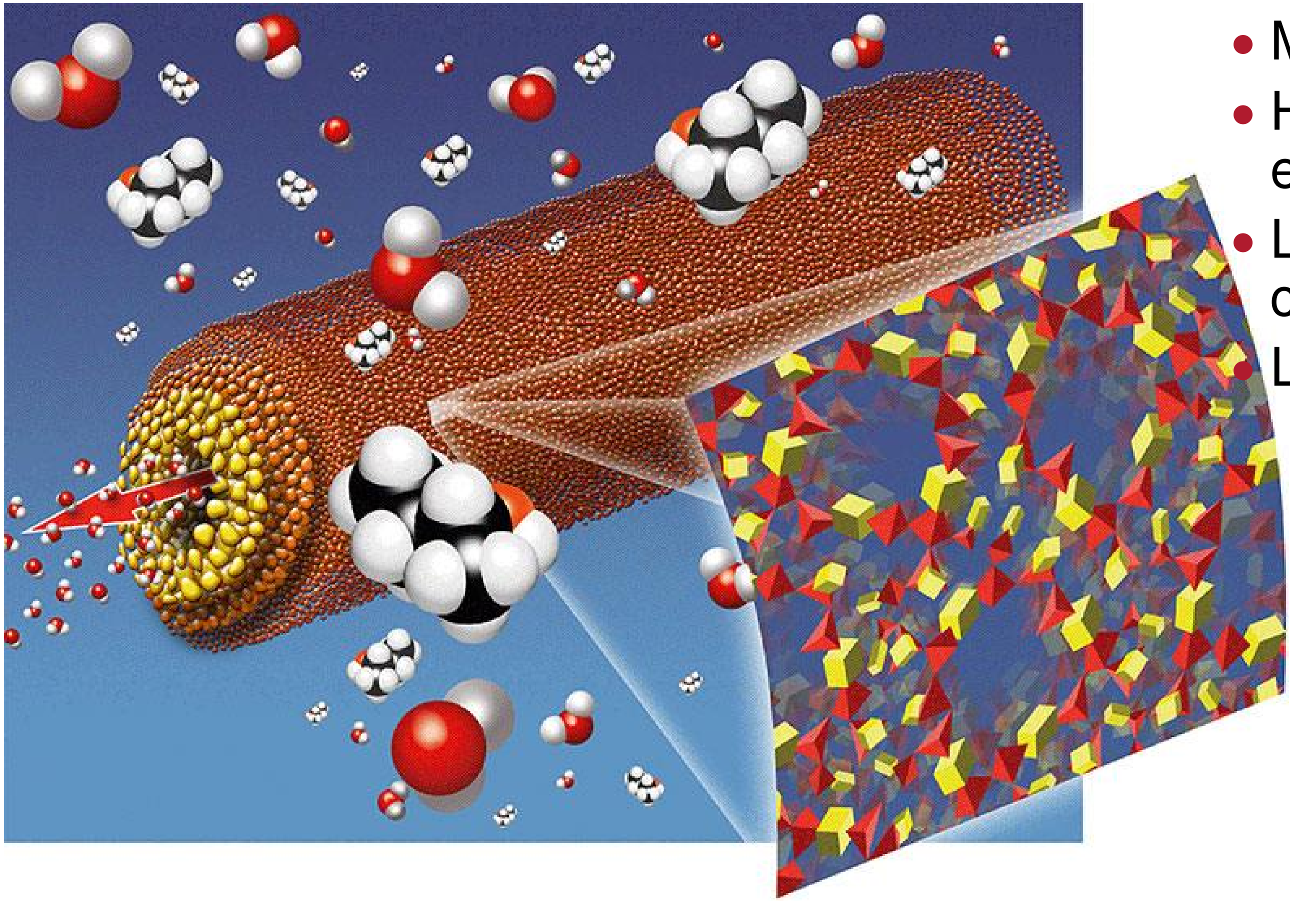
T = 190 C

Performance hybrid membranes (3)



Feed = 5 wt.% water in solvent

Origins of stability



- More stable bonds
- Higher crack propagation energy
- Lower surface diffusion coefficient
- Lower solubility

ECN

Hybrid membrane in the press

Over 1700 hits on Chem Commun in February 2008 alone!

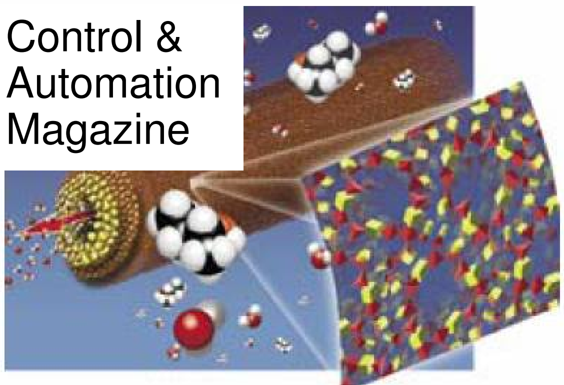
NRC
Chem Engineering
MIT Tech Review
Chem Processing

BAANBREKENDE NIEUWE NANOZEEF

voor zuinige industriële scheidingsprocessen

Onderzoekers van het MESA+ Instituut voor Nanotechnologie van de Universiteit Twente en het van 't Hoff Instituut van de Universiteit van Amsterdam hebben een nieuw type membraan ontwikkeld dat grote potentie heeft voor toepassing in industriële scheidingsprocessen. Tests bij het Energieonderzoekcentrum Nederland (ECN) tonen aan dat het membraan meer dan een jaar lang bestand is tegen blootstelling aan hoge temperaturen.

Control & Automation Magazine



Artistieke weergave van de nanozeef zoals gepubliceerd door het wetenschappelijke tijdschrift Chemical Communications.

'Verbazingwekkend stabiel'

Nanosieves that survive extreme conditions c

Energy saving sieves

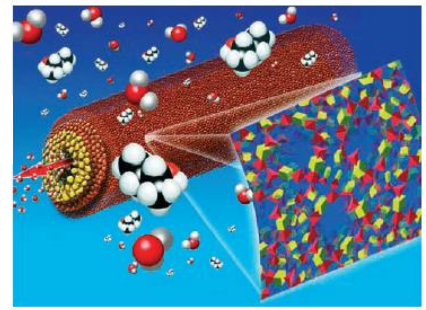
Dutch scientists have made molecular sieves that are stable at high temperatures for over a year. The stability of these nanosieves means that they could replace

Chem Tech

industrial separation. However, until now the silica-based membranes could not be used in industrial applications because they would not operate both at high temperatures and in the presence of water. This is because the Si–O–Si bonds in the silica are open to attack by water.

Hessel Castricum from the University of Twente and co-workers have replaced some of the Si–O–Si bonds with organic linkers such as –Si–CH_2–CH_2–Si– that do not hydrolyse. The materials produced act as effective sieves even after 18 months at very high operating temperatures.

At the moment, industrial



separations involve techniques such as distillation that require large amounts of energy and can have efficiencies as low as 10%. Instead of distilling to obtain a pure product, a nanosieve could be used to filter small molecules, such as water or hydrogen, leaving behind the larger ones. Biofuels, such as bioalcohols,

Organic linkers between silicon atoms prevent water attacking the sieves

Reference
H L Castricum *et al*, *Chem. Commun.*, 2008, 1103 (DOI: 10.1039/b718082a)

could be dried using this technology. According to Castricum, the vast energy needs of current distillation plants are proving to be a major stumbling block in implementing biofuel technologies.

Henk Verweij, an expert in ceramic engineering from Ohio State University, Columbus, US, said that the membranes 'could be used for dehydration of industrial alcohol-water mixtures at temperatures up to 150°C'.

Castricum said that his nanosieves have removed the 'serious limitations for industry to become involved in membrane technology and it should be seen as a highly energy-efficient alternative for existing processes.'

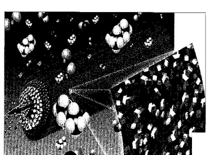
'The next challenges are to confirm our findings in an industrial-scale pilot test and to develop materials that withstand even more extreme conditions, such as strong bases and very high temperatures,' he said. *Ruth Doherty*

Een bepaald slag atleten zal reikhalzend uitkijken naar S107.

WATERBESTENDIG MEMBRAAN

Geslaagd huwelijk tussen organisch en anorganisch.

Nederlandse onderzoekers hebben een nanoporeus membraan ontwikkeld waarmee je water kunt verwijderen uit een hete oplosmiddelstroom, zonder dat het membraan zelf wordt aangetast. Ze denken er onder meer biobrandstoffen mee te kunnen ontwateren, iets waar nu nog een energievretende destillatie voor nodig is. Op de onlangs in *Chemical Communications* beschreven vinding is wereldwijd octrooi aangevraagd.



Het membraan is een moleculaire zeef voor water.

bijvoorbeeld methylgroepen aan toe te voegen. Onderzoekers van het Twentse MESA+ Instituut, ECN in Petten en de UvA hebben dit idee nu verder uitgewerkt. Ze probeerden een materiaal op siliciumbasis te maken met zo weinig mogelijk siloxaanbindingen (Si-O-Si) en zo veel mogelijk silylbindingen (Si-C), die

durig in contact komt met water van 60 °C.

C2W

Geen bottleneck meer voor keramische membranen

MATERIAALKUNDE Vernieuwend genoeg behouden membranen gecoat met 'hybride silica' hun selectiviteit lange tijd en bij hoge temperaturen.

Silica in membraancoatings lost een beetje op in water en sluit vervolgens weer niet. Hierdoor verandert de poriestructuur van het membraan, met als gevolg dat de selectiviteit verloren gaat.

Tech Weekblad

TECHNOLOGIE

Doorbraak in keramische membranen

Keramische membranen gelden als potentieel veelbelovend om scheidingen in de petrochemische industrie energiezuiniger te maken. Onderzoekers van

Het totale energieverbruik in de petrochemische industrie in Nederland was in 2000 ongeveer 880 petajoule, volgens gegevens van ECN. Veertig procent hiervan komt voor rekening van scheidingsprocessen. In de procesindustrie wordt vooral veel gedestil... om stof-

De poriegrootte en ... laag is afhankelijk van de ... Voor gasscheiding bevat de ... voorbeeld poriën in de orde van ... enkele Ångströms (1 Ångström = ... nanometer = 10^{-10} meter). Of ... bestaat uit een zeer dunne laa...

Petrochem

Next steps

- FOCUS: IMPLEMENTATION

- State of the art membrane
  - Determine application window pH, H_2O content, solvents
  - Create consortium for commercialisation: end user(s), membrane producer(s), system integrator(s), supplier(s) enabling parts.
  - Definition launching application(s).

- Further development:
  - Reduce pore size: H_2O-EtOH, and hydrogen separation
  - Increase pore size: nanofiltration

Next step: $1m^2$ field test

Acknowledgements

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Thank you for your attention

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Chem. Commun., 2008, 1103 - 5, DOI: 10.1039/b718082a
J. Mater. Chem., 2008, 18, 2150 - 8, DOI: 10.1039/b801972j
J. Sol-Gel Sci Techn, 2008, DOI: 10.1007/s10971-008-1742-z
J. Mem. Sci, 2008, in preparation
PLUS MORE TO COME!

Patent: WO2007081212