Treating Coal-Bed Methane Produced Water for Beneficial Use by MFI Zeolite Membranes

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DOE-PERF Water Program Review Meeting, Annapolis, MD, Nov. 2005.

1. OVERVIEW

- **Grant: NETL/DOE (DE-FC26-04NT15548)**
  - *DoE project manager: Jesse Garcia (Tulsa)*
- **Timeline**
  - *Project start date: October 1, 2004*
  - *Project end date: September 30, 2007*
  - *Percent complete: ~32%*
- **Budget/Total Project Funding**
  - *DOE: $855,204*
  - *Contractor: $285,068*

Funding received in FY04: $354,075
Funding for FY05: $365,283

- **Project Goal**
  - Demonstrate a new technology of reverse osmosis through molecular sieve zeolite membranes for efficiently treating the CBM produced brines for beneficial use.

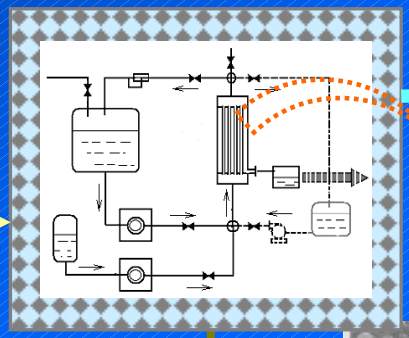
2. SCOPE & APPROACH

Fundamental study for development of chemically stable *zeolite membranes for reverse osmosis* (RO) purification of coal-bed methane produced water for beneficial use. Project includes three phases:

- Phase 1 (FY05): Understand the mass transport behaviors of water and ions in zeolite membrane and the effects of operation parameters on the RO performance. (**COMPLETE**)
- Phase 2 (FY06): Optimize the RO operation conditions and effectively improve membrane. (**ON-GOING**)
- Phase 3 (FY07): Long-term laboratory RO test using a 0.1-m^2 tubular membrane unit for technical evaluation.

2.1 TECHNICAL APPROACH & BENEFITS

SEPARATION



Organic-containing CBM produced brine

Clean Water

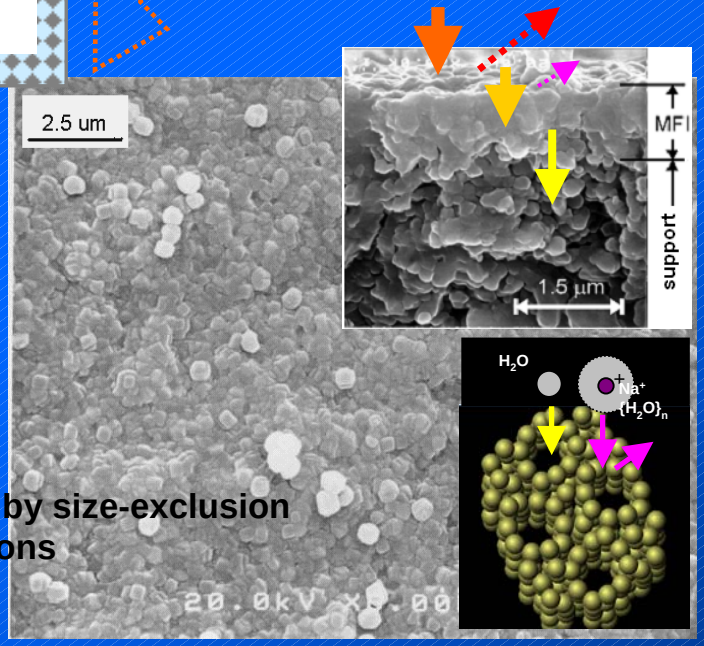
(Beneficial uses)

Residual

Disposal – reduced volume

Molecular sieve zeolites:

- Crystal: excellent chemical, mechanical, and thermal stabilities.
- Sub-nanometer pores suitable for molecular/ion separation.



Desalination by size-exclusion of hydrated ions

Benefits:

- Mitigate environmental liability and relieve financial burden caused by produced water in oil and gas production.
- Ease water shortage in NM and southwest arid regions.

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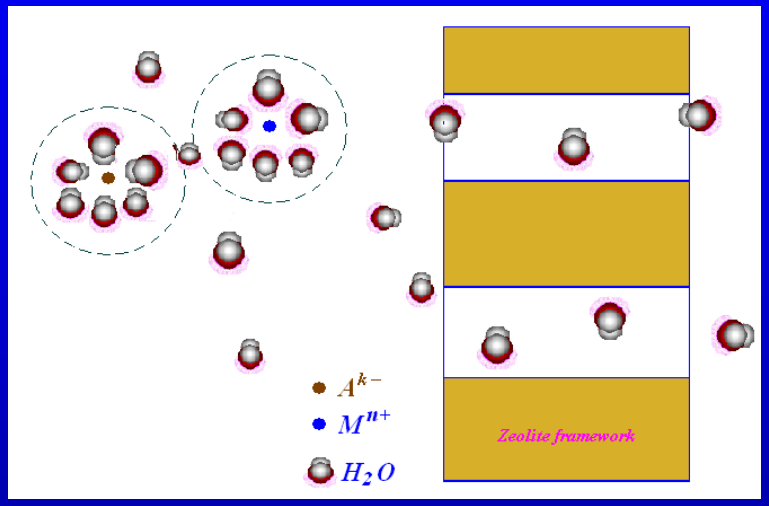
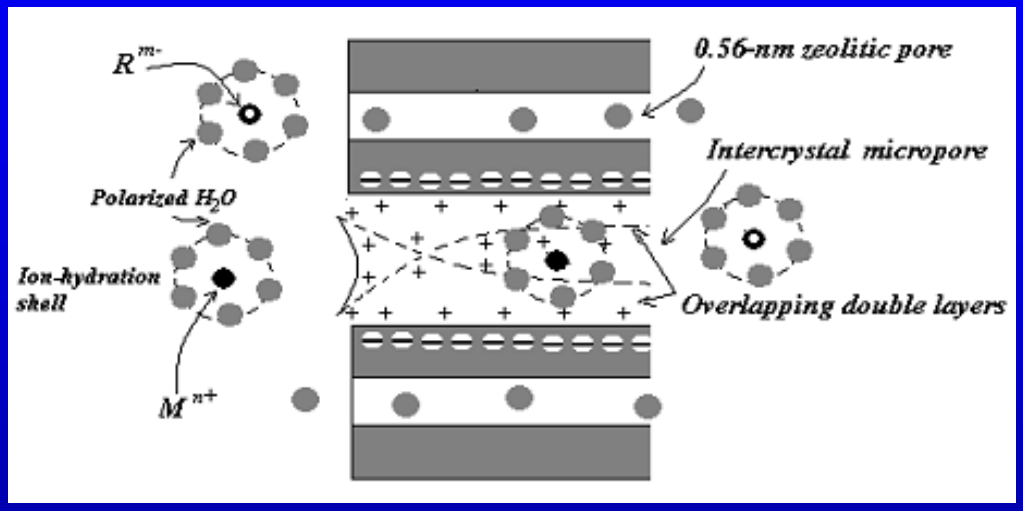
2.2 DESALINATION MECHANISM

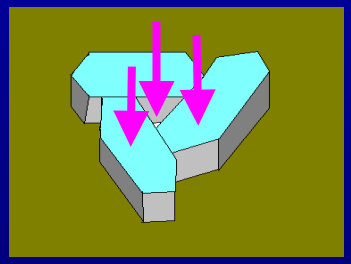
MFI-type zeolite used in this project: pore size 0.55 nm





Free permeation of water: molecular size of water much smaller than zeolitic pores;
Rejection of ions: hydrated ion size much larger than zeolitic pores.

Effect of the nanoscale intercrystalline pores: decreases ion rejection rate, especially for high TDS brines.



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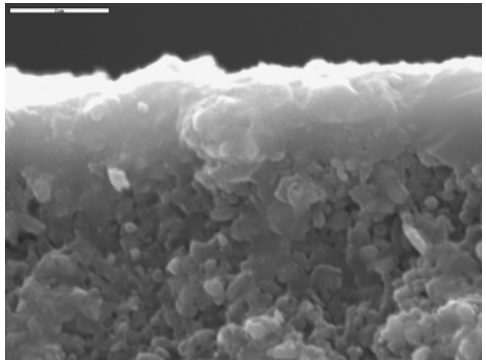
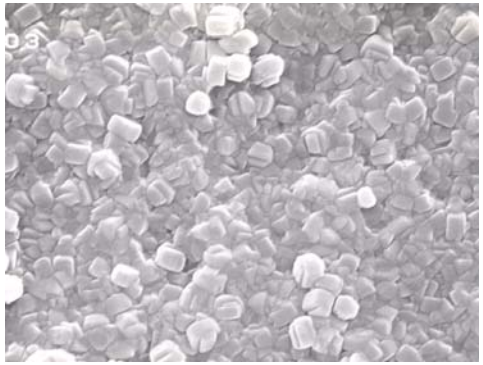
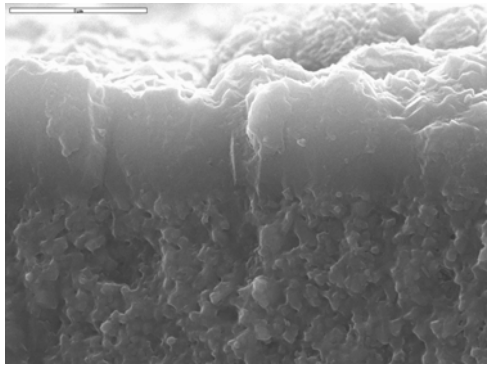
3. CURRENT STATUS

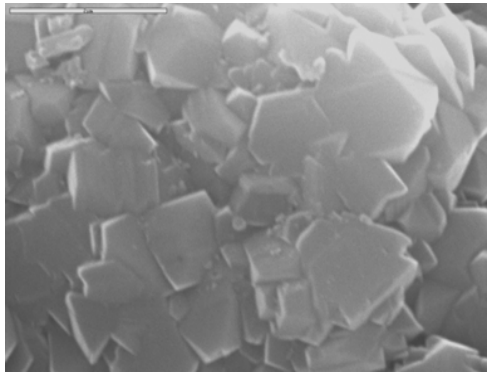
3.1 High quality zeolite membranes synthesized



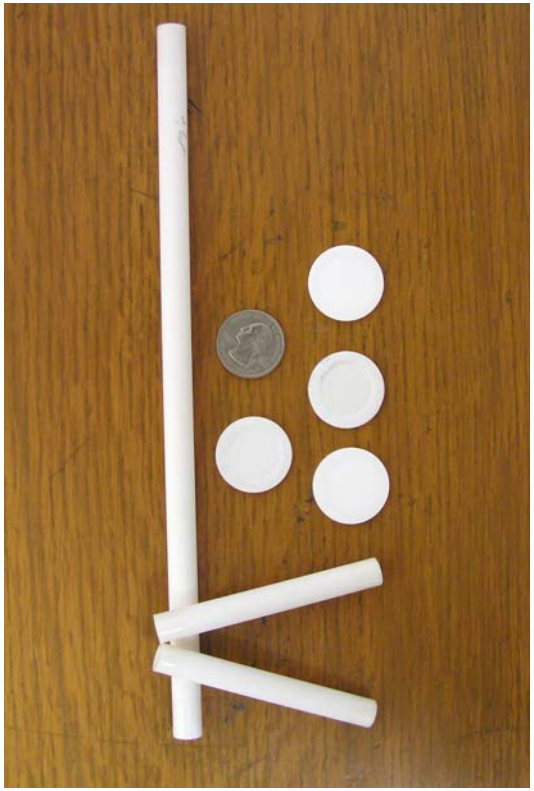


MFI membrane
Pore size: 0.55nm
Hydrophobic





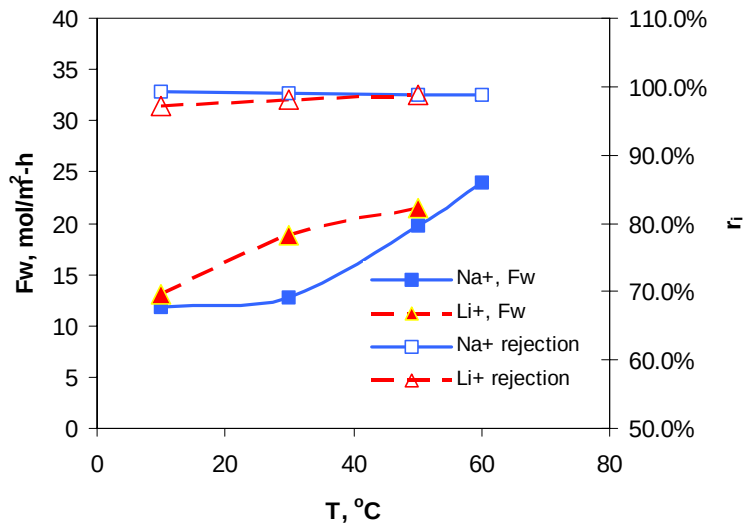
NaY (FAU) membrane
Pore size 0.74 nm
Hydrophilic



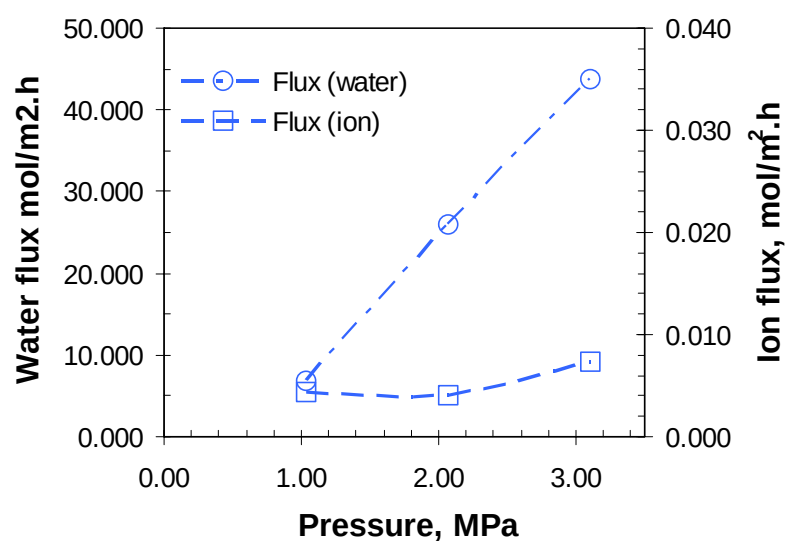
Tubular and disc membranes
Tubes: Pall Corp.

3.2 EFFECTS OF OPERATING TEMPERATURE AND PRESSURE

Effect of temperature



Effect of applied pressure

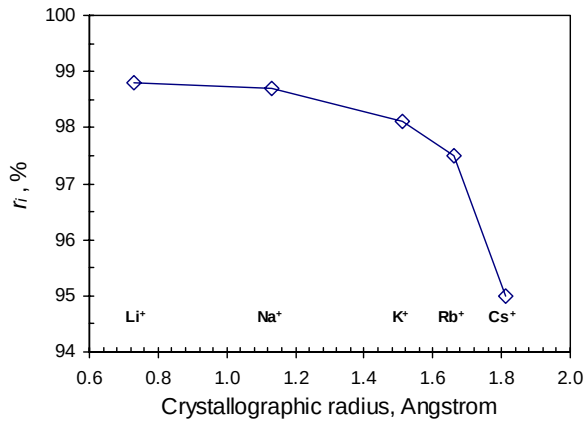


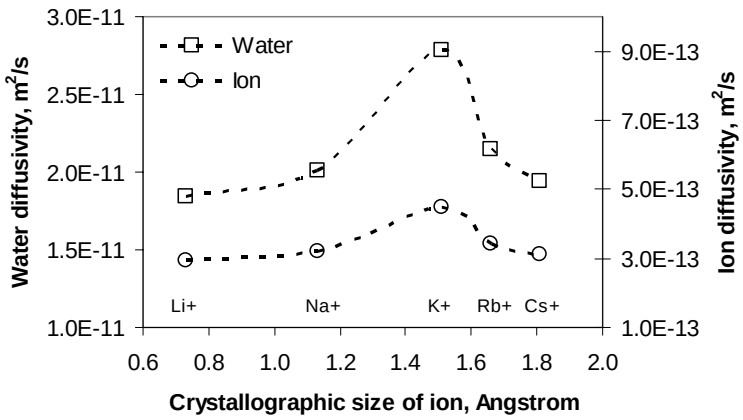
ADVANTAGES: Increasing temperature and pressure significantly enhances water flux while maintaining high ion rejection.

3.3 ION AND WATER TRANSPORT MODEL

$$J_w = -K_w \cdot \frac{dp}{d\delta} = K_w \cdot \frac{[p_f - p_p - \Delta\pi]}{\delta}$$

$$J_{ion} = J_{i,1} = J_{i,2} = \left[D^0_{i,C} \ \exp\left(\frac{-E_{i,c}}{RT} \right) \right] \cdot \left[K' \cdot \exp\left(\frac{-\Delta E_{i/w}}{RT} \right) \right] \cdot \left[\frac{C_{i,f}}{\delta} \right] = \alpha_{i,1} \cdot D_{i,c} \cdot \frac{C_{i,f}}{\delta}$$

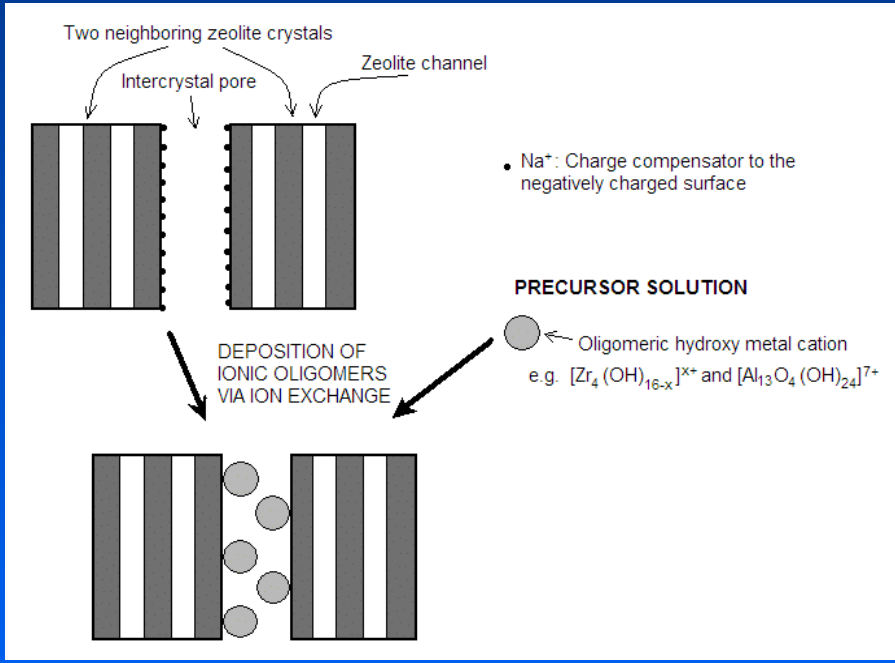


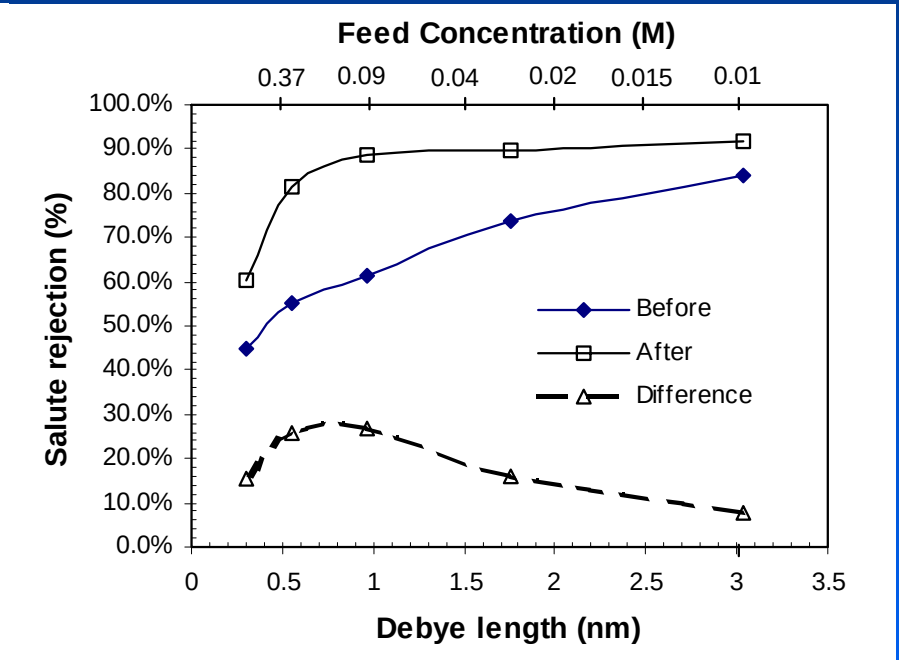


High rejection for alkali metal ions; multivalent ions are easier to be separated by size exclusion due to higher charge density (hence larger hydrated ions).

3.4 PRELIMINARY RESULTS ON MEMBRANE IMPROVEMENT

(PHASE II)





Online healing: deposition of metal ion oligomers in intercrystal pores.

RO performance: before and after modification.

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3.5 COMPARISON WITH TRADITIONAL RO MEMBRANES

BASED ON RO RESULTS FOR CBM PRODUCED WATER FROM FARMINGTON, NM

	Properties	Polymer Membrane	Zeolite membrane
Advantages	Organic resistance	Poor	Excellent
	Organic rejection	Incapable of	Good (>90% BETX)
	Ion rejection	Good (>95%)	Good (>95%, 1%TDS)
	Applicable TDS level	Low (<4%)	High (>10%TDS)
	Membrane regeneration	NO	YES
	Lifetime	Short (< 3 mon)	Long (> 5yr ?)
	Chemical stability	Unstable in low pH	Stable: acidic to basic
	Operating pressure	>800 Psi	< 500 Psi
	Thermal stability	Poor	Excellent
Issues	Water flux	>5 kg/h.m^2	~1.0 kg/h.m^2 (r_i>80%)
	Membrane cost	Low	High

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CONCLUSION/PLANS (Phase II)

- Zeolite membranes are capable of purifying oil and gas field brines.
- Enhance water flux and ion rejection: optimize operating conditions and improve membrane:
  - Temperature and pressure
  - Thinner membranes
  - Intercrystal pore repairing/minimization

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TRANSFER OF KNOWLEDGE

PUBLICATIONS in leading journals

- L. Li, J. Dong, T.M. Nenoff, Transport of Alkali Metal Ions in MFI Zeolite Membranes during Reverse Osmosis. *Environmental Science & Technology*, *submitted* (2005).
- X. Gu, J. Dong, T. M. Nenoff , D. E. Ozokwelu, Separation of *p*-Xylene from Multicomponent Vapor Mixtures Using Tubular MFI Zeolite Membranes. *Journal of Membrane Science, revised after peer reviewed* (2005).
- J. Zhang, J. Dong, M. Luo, H. Xiao, S. Murad, R. A. Normann, Zeolite-Fiber Integrated Optical Chemical Sensors for Detection of Dissolved Organics in Water. *Langmuir*, 21 (2005), 8609.
- H. Xiao, J. Zhang, J. Dong. M. Luo, R. Lee, V. Romero, Synthesis of MFI zeolite films on optical fibers for detection of chemical vapors, *Optics Letters*, 30, 11(2005), 1270.
- X. Gu, J. Zhang, J. Dong, T.M. Nenoff, A Platinum-Cobalt-Loaded NaY Zeolite Membrane for Nonoxidative Conversion of Methane to Higher Hydrocarbons and Hydrogen. *Catalysis Letters*, 102, 1-2 (2005), 9.
- X. Gu, J. Dong, T.M. Nenoff, Synthesis of defect-free FAU-type zeolite membranes and separation for dry and moist CO_2/N_2 mixtures. *Ind. Eng. Chem. Res.*, 44 (2005), 937.
- * L. Li, J. Dong, T.M. Nenoff, R. Lee, Desalination by Reverse Osmosis Using MFI Zeolite Membranes. *Journal of Membrane Science*, 243(2004) 401.

PRESENTATIONS in national conferences

- J. Dong, L. Li, H. Xiao, R. Lee, “Treating Coal-Bed Methane Produced Water for Beneficial Use By Reverse Osmosis through Zeolite Membranes”, Ground Water Protection Council (GWPC) Annual Meeting, Portland, OR, September 24 – 28, 2005.
- * L. Li, A. Ryan, T.M. Nenoff, J. Dong, R. Lee, Purification of Coal-Bed Methane Produced Water by Zeolite Membranes. *SPE Annual Meeting (Paper # 89892)*, Houston, TX, Sept. 27 – 29, 2004.

RELATIONSHIPS TO OTHER DOE PROJECTS

- **Membrane/thin film synthesis technology developed in this project has been used in the following DOE funded projects:**
  - Zeolite membranes for WGS membrane reactors for hydrogen production (EERE/DOE)
  - Catalytic membranes for conversion of biomass-derived stocks to hydrogen (HNEI/DOE & EERE through Sandia)
  - Zeolite-integrated chemical sensors for clean energy technology and environmental monitoring (NETL/DOE & WERC)
  - Zeolite membranes for xylene separation (OIT/DOE)
  - Zeolite membranes for CO_2 separation (NETL/DOE)

THANK YOU
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