Radiochemistry Webinars

Separation of Xenon and Krypton from nuclear re-processing using Open Framework Materials

In Cooperation with our University Partners
Meet the Presenter...

Dr. Praveen K. Thallapally is a chief scientist at the Pacific Northwest National Laboratory. He obtained his PhD in 2003 from the University of Hyderabad working with Prof. Gautam R. Desiraju in the area of Crystal Engineering of organic and metal organic solids. He moved to the University of Missouri Columbia as a post-doctoral fellow working with Prof. Jerry L. Atwood in the area of supramolecular chemistry, gas storage and separation. He leads research efforts in the design of porous materials for energy conversion, catalysis, immobilization of radionuclides and electro-optic responsive metal organic frameworks. He published more than 120 research articles with an H-index of 45. He is an advisory board member for Crystal Growth & Design, CrystEngComm and Journal of Coordination Chemistry.

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Interns, Postdocs and Co-workers

- Mr. Paul Reiss (Intern, UK), Dr. Carlos Fernandez, Todd Schaef, Dr. Nune Satish
- Prof. Wen Zhang, China

Not shown
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- Prof. Atwood Columbia, MO
- Prof. Zaworotko Ireland
- Prof. Cooper UK
- Prof. Parise USA

Collaborators:
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- Prof. Maciej Haranczyk, Berkeley

Programmatic and Technical Advise:
- Dr. Denis Strachan & Dr. Pete McGrail, PNNL
- Dr. Troy Garn, Dr. Mitch Greenhalgh & Dr. Amy K. Welty (not shown), INL
Outline

- Definitions
- History of Xenon and Krypton
- Nuclear re-processing
- Porous materials – Metal organic frameworks
- Synthesis and characterization
- Adsorption and separation
- Conclusion
- Questions?
**Definitions**

**Porous/Pores:** Tiny spaces or holes through which liquid or gas molecules penetrate (ultramicropore < 0.5 nm, micropore >0.5 - 2 nm, mesopore 2 – 5 nm, or macropore >5nm)

**Van der Waals Forces:** When two atoms come close to each other, a slight interaction between them causing polarity and slight attraction

- Electrons
+ Positive nucleus
Definitions

**Electrostatic Attraction or Hydrogen bonding:** attraction between two polar groups when hydrogen atom covalently bound to a highly electronegative atom

**Hydrogen bonding strength**

- $\text{F}^-\text{H}\cdots\text{F}$ (38.0 kcal/mol)
- $\text{O}^-\text{H}\cdots\text{N}$ (6.0 kcal/mol)
- $\text{O}^-\text{H}\cdots\text{O}$ (5.0 kcal/mol)
- $\text{N}^-\text{H}\cdots\text{N}$ (3.1 kcal/mol)
- $\text{N}^-\text{H}\cdots\text{O}$ (1.9 kcal/mol)

**Coordination complex** in which each metal atom connected to multiple molecules or ligands depending on their coordination number

\[
2 \text{R-COOH} + \text{Cu(OH)}_2 \rightarrow \text{R-COO-M-COO-R} > 100 \text{ kcal/mol}
\]
**Definitions**

**Adsorption:** is phenomenon in which gas/liquid molecules are attached to solid surface by intermolecular interactions.

**Physical adsorption:** attached to solid surface by weaker interactions between solid and gas/liquid.

**Chemical Adsorption:** Stronger interactions between the solid and gas/liquid.

**Desorption** in which the adsorbed gas/liquid released from the surface by heating or vacuum.
Definitions

**Adsorption isotherm**: A graph between the amount of gas/vapor adsorbed on a solid and pressure at constant temperature.

**Breakthrough Curve** is a plot of the composition at the outlet against time, relative to the initial inlet composition. The breakthrough curves can be used as a rapid method to compare the potential performance of new materials for gas separation applications.

\[
\text{Breakthrough capacity (} q \text{ in mmol/kg)} = \frac{C_{\text{vol}}}{M \times T \times g} \times 10^6
\]

Selectivity of Gas A over B \( S_{AB} = \frac{x_A}{y_A} \times \frac{y_B}{x_B} \)

\( x_A \) and \( x_B \) are the mole fractions of gases A and B in the adsorbed phase, and \( y_A \) and \( y_B \) are the mole fractions of gases A and B in the bulk phase,
History of Xenon and Krypton

- Xenon and Krypton – discovered by Sir William Ramsay and Morris Travers 1898
- Xenon and Krypton are odorless, colorless, tasteless and chemically non reactive
- In 1962 Neil Bartlett discovered Xe and Kr will react with fluorine to form fluorine derivatives.

<table>
<thead>
<tr>
<th>Xenon</th>
<th>Krypton</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>54</td>
</tr>
<tr>
<td>Atomic mass</td>
<td>131.29 g.mol$^{-1}$</td>
</tr>
<tr>
<td>Density</td>
<td>5.9 x10$^{-3}$g.cm$^{-3}$ at 20°C</td>
</tr>
<tr>
<td>Melting point</td>
<td>-112 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>-107 °C</td>
</tr>
<tr>
<td>Diameter</td>
<td>0.4 nm</td>
</tr>
</tbody>
</table>
Source of Xenon and Krypton

- Xenon and Krypton occur naturally in the atmosphere at 0.087 ppmv (Xe) and 114 ppm (Kr)
- Xe has nine and Kr has six naturally occurring stable isotopes.

Radioactive Xe and Kr

- Fission of uranium, plutonium or other radioactive decay of fission products
- Production of medical isotopes
- Nuclear accidents - Fukushima Daiichi Nuclear Power Plant in Japan
- Dissolution of the spent fuel in nuclear reprocessing

- Radioactive Xe isotopes are monitored around the globe to detect nuclear explosions
- These systems detected and tracked Xe isotopes from the Japanese nuclear accident
Statistic on spent fuel

- Spent fuel is a nuclear fuel that is irradiated in the nuclear reactor

- Love It or Hate It We Have It: What to do with It is the Issue

- We have about 70,000 tonnes

- Current reactors will produce 60,000 tonnes more over their lifetimes
Reprocessing the spent fuel

- Spent fuel can be reprocessed to recover fissile and fertile materials to provide fresh fuel to new and existing nuclear plants saving up to 30% of the natural uranium otherwise required.

- Reduce the volume of material to be disposed of as high-level waste to about one-fifth.

- In addition, the level of radioactivity in the waste from reprocessing is much smaller compared to before reprocessing.

Separations of non-burnable volatile fission products and lesser actinides
Reprocessing flow diagram

Mass Basis: 1 kg SNF; 55 GWD/MTIH; 5 year Cooling

Provided by R. Jubin, ORNL

129I 1.7 x 10^7 y
131I 8.04 d
90Sr 29 y
81Kr 2.1 x 10^5 y
133Xe days
Separations and applications

- Capture of Xe provides an economic incentive

- **High purity of Xe**
  - Buildings - Commercial lighting
  - Automotive - Head lights
  - Space Industry - Propellant
  - Medical - Anesthesia, Imaging
  - Science - NMR

- **High Purity of Kr**
  - Insulation - Efficiency is 6 times higher than normal windows
  - Flat panel display manufacturing
Objective and existing technologies

- **Objective:** The objective is to develop and test alternative materials to capture volatile radioactive gas components (most specifically Kr) released during Used Nuclear Fuel Reprocessing operations.

- **Existing Technology**
  - Cryogenic distillation to remove Xe and Kr
    - Projected to be expensive
    - Potential to accumulate O₃ due to radiolysis of O₂ ⇒ Explosion hazardous

- **Immobilization**
  - Elevated pressure in a stainless steel canisters
  - $^{85}\text{Kr}$ decay product Rb is a liquid at storage temperatures
  - Corrosive to storage canisters

$5,000$ per kilogram
Alternate materials/methods

- **Porous Materials**
  - Separation at higher temperatures
  - Remove Xe and Kr in separate steps
  - Remove Xe at ambient temperature
    - Recover process costs by selling Xe?
  - Remove Kr at near room temperature

- **Porous Materials allow**
  - More gas to be stored in the canister at lower pressures
  - The decay product Rb would be isolated from the metal canister
  - Porous materials have capacities 3 to 10 times those of currently used materials. For eg. CO₂, H₂ and Natural gas

Thallapally et. al., Chem Commun., 2013
Porous materials

**Organic Solids**

**Organic**

**Prussian Blue/Zeolites**

**Inorganic**

**MOF’s/COFs**

**Hybrid**

- Windisch et. al., Spe. Chem. 2009
- Windisch et. al., Spe. Chem. 2010
- Thallapally et. al., Inorg. Chem., 2010
- Thallapally et. al., Cryst. Eng. Comm., 2010

- Thallapally et. al., Angew. Chem., 2005
- Thallapally et. al., Angew Chem., 2006
- Thallapally et. al., J. Am. Chem. Soc. 2007
- Thallapally et. al., Chem. Mat., 2007
- Thallapally et. al., Angew Chem., 2009
- Thallapally et. al., J. Am. Chem. Soc., 2009
- Thallapally et. al., Chem Comm 2010
- Thallapally et. al., Chem Comm, 2010
- Thallapally et. al., Chem Comm 2011
- Thallapally et. al., Chem Comm., 2012
- Thallapally et. al., Chem Comm 2012

- McKinley et. al., Angew Chem., 2005
- McKinley et. al., Chem. Comm., 2006
- Thallapally et. al., Inorg. Chem., 2009
- Thallapally et. al., Chem. Comm., 2010
- Thallapally et. al., Chem. Comm., 2010
- Thallapally et. al., Chem Comm., 2010
- Thallapally et. al., Chem Comm., 2011
- Harvey et. al., J. Sep. Sci. 2011
- Wang et. al., Chem Comm 2013
- Kui et. al., Chem. Mat., 2013
(a) non-porous
(b) discrete voids
(c) porous molecular crystal without collapse of the host lattice.
Organic Solids 101
Design Principles

[Chemical structures and diagrams related to organic solids and design principles]
Micro Porous MOFs

The use of multiple metal ions in a cluster bridged by multiple coordinating ligands tends to enhance the robustness of the MOF.

Yaghi et. al., Science 1998
Advantages

- MOFs are hybrid crystalline porous solids with a vast array of topologies constructed from metal ion clusters and organic linkers.
- More than 20,000 MOF structures are known to date.
- The properties of MOFs are easier to tune synthetically than those of other porous compounds.
- The MOF structures are controllable to certain degree by the choice of molecular building blocks.

Yaghi et. al., Science 2013, 974; Kitagawa et. al., Angew Chem. 2002; Ferey et. al., Science 2002
Advantages and disadvantages

- Long cycle stability 500 – 2000
- More than 5,000 experimental and 130,000 hypothetical MOF structures are known to date
- Possess much higher specific surface area (~8,000 m$^2$/g) than possible in any other traditional crystalline material

Disadvantages

- Stability 300 - 900°C
- Limited quantities
Synthesis protocol

- MOFs are constructed from precursor chemicals that in most cases are readily available.

- Mild synthesis conditions provide options for in-house production as desired.

- MOFs can be made in many different forms as needed:
  - Bulk powders
  - Nanoparticles
  - Fibers
  - Gels
Batch process

- **Solution 1**
- **Solution 2**
- **Reaction Vessel @100°C**
- **Hot Plate**
- **Magnetic Stir bar**
- **Reaction mixture**
- **Wash/soak with solvent**

**Solvothermal or Hydrothermal**

- Solution (organic linkers)
- Solution (metal connector)

- Crystallization/precipitation
- Filtration/Drying
- Characterization (XRD, BET and so on)

- Solvent Recycle
Physical and chemical properties

- **Gas composition in nuclear re-processing plants**

  - Xe: 400 ppm
  - Kr: 40 ppm
  - Ar: 0.9%
  - N₂: 78%
  - O₂: 21%
  - H₂O: very low
  - O=C=O: 0.03%

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Ideal adsorbent

- **Ideal sorbent characteristics for Xe/Kr sep from re-processing con.**

- **High Capacity** (Xe or Kr)
- **High Selectivity** (N₂, O₂, H₂O, Ar, CO₂ etc.)
- **Faster Kinetics**
- **Stability/Radiation over 1000 cycles**

Types of MOFs studied

1. MOF-5, a prototype
2. MOFs functionalized with polar groups
3. MOFs containing open metal sites
4. Hydrophobic MOFs with small pore size
5. MOFs impregnated with Ag$^0$ nanoparticles

- Role of surface area
- Open metal sites
- Small pores/polar groups
- Nanoparticles

Thallapally, Cooper et al., Nature Materials., 13, 954, 2014
Thallapally et al., Chem. Comm., 2012, 48, 347
MOF-5 synthesis and characterization

*Mol For: Zn₄O(BDC)₃*
Synthesis of a Mdobdc family of MOFs

Methanol/water/heatin

M(NO₃)₂
M = Zn, Ni, Co and Mg

[M₂(DOBDC)(H₂O)₂]·8H₂O

Milligram scale

Milligram

Scale up

PNNL engineered form

Yaghi et. al., PNAS., 2006
Characterization of Mdobdc MOF

- Identical PXRD indicate the successful synthesis and identical topology
- Thermogravimetric analysis indicate ~30% of weight loss between RT to 250 °C
- 1200 m²/g surface area
36 mass% at 100 kPa (1 bar)
Reversible adsorption and desorption
Selective towards CO₂ over N₂
Better CO₂ capacity than any other sorbent
Gravimetric gas analyzer

- Pressure/gas composition changed and held constant to set point $P_n$
- Weight data is acquired and analyzed in real time to determine the equilibrium uptake
- Equilibrium points are collected and plotted as an isotherm
What about Xenon and Krypton MOF-5 Vs Nidobdc

- **MOF-5 to NiDOBDC**
- **Doubled Xe uptake**
  - From 28% @ 1 bar
    - To 56% @ 1 bar
    - Reversible at all temperatures
    - Increase capacity at lower temperatures

- Active site playing a key role in gas adsorption at low pressure than surface area.

Thallapally et al., Chem. Comm., 2012
**Nidobdc MOF**

- Corresponds to seven Xe per cavity.
- Highly selective to Xe over Kr, N₂

- The only mechanism for Xenon to interact is based on its polarizability.

- Metal cations are very polarizing, which may enhance the interaction with polarizable adsorbents.

- Additionally, high surface area, uniform porosity, and high diffusivity make NiDOBDC more attractive.

- The ability to tune the properties by replacing nickel with another transition metal center (Mg, Co, Zn and Mn) is advantageous compared to other materials.

Thallapally et. al., Chem. Comm., 2012, 48, 347
In-situ XRD on Nidobdc with Xe/Kr flow NSLS/PETRA III

Breakthrough measurements apparatus

Table 1. Properties of the Ni/DOBDC Pellet

<table>
<thead>
<tr>
<th>property</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pressed pressure</td>
<td>12 MPa</td>
</tr>
<tr>
<td>size</td>
<td>600–850 μm</td>
</tr>
<tr>
<td>pellet density</td>
<td>0.78 g/cm³</td>
</tr>
<tr>
<td>packing density</td>
<td>0.40 g/cm³</td>
</tr>
<tr>
<td>BET surface area</td>
<td>1147 m²/g</td>
</tr>
<tr>
<td>original weight</td>
<td>1.51 g</td>
</tr>
<tr>
<td>activated weight</td>
<td>1.01 g</td>
</tr>
</tbody>
</table>

Thallapally et. al., Langmuir 2012, 28, 11584
Nidobdc pellet characterization

- PXRD confirms the crystallinity of the sample
- No amorphization upon pressurization
- Reduced surface area of the pellets compared to powder
- Uptake of Xe/Kr using breakthrough matches with static method

Thallapally et al., Langmuir 2012, 28, 11584
Single column experiments with off-gas mixture

Air = 400 ppm Xe, 40 ppm Kr, 78% N₂, 21% O₂, 0.9% Ar, 0.03% CO₂ etc

- He flow rate and the flow rate of Xe and Kr in air is 20 sccm.
- NiDOBDC adsorbs Xenon preferentially over other gases
- >95% of Xenon is captured from air using NiDOBDC
- Ni/DOBDC is able to separate 400 ppm Xe from 40 ppm Kr mixture in air with a Xe/Kr overall selectivity of 7.3.
- The uniform cylindrical pores are believed to be favorable to maximize the Xe/Ke selectivity

Thallapally et al., Langmuir 2012, 28, 11584
Two-column breakthrough experiments with off-gas mixture

Air = 400 ppm Xe, 40 ppm Kr, 78% N₂, 21% O₂, 0.9% Ar, 0.03% CO₂ etc

- A two-bed technique to remove and separate
  - Bed 1 remove Xe from air
    • NiDOBDC MOF
    • Yields air with Kr
  - Bed 2 remove Kr
    • Yields air without Xe and Kr
    • Off-gas can be released

- Results
  - Air: 400 ppmV Xe, 40 ppmV Kr
  - Removal of Xe first (Bed 1) removes competition on Bed 2
  - NiDOBDC capacity
    • 0.24 mmol/kg w/ Xe
    • 0.61 mmol/kg w/o Xe
Effect of $\gamma$ radiation ($^{60}$Co)

- The goal is to deliver the same amount of radiation exposure to the material using $^{60}$Co as would be delivered by the $^{85}$Kr.
- Needed $1.4 \times 10^{13}$ R
- Max about $7 \times 10^{6}$ R

This view shows the distance between the source and the collimator.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dose</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>960 000</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1920 000</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>3840 000</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>6720 000</td>
<td>7</td>
</tr>
</tbody>
</table>
Surface area measurement on radiation irradiated samples

- Only a minor change in the surface area with radiation
- Due to the presence of an impurity
Xenon and Krypton loading

- Slightly reduced Xe/Kr at 1 bar and RT
- Might be due to the 10% of impurity (Nickel formate) in the samples studied
- Nickel formate was confirmed from the XRD powder patterns.
Techno economic evaluation of MOF-based separation

Techno-economic considerations for noble gas capture from UNF processing

<table>
<thead>
<tr>
<th>Process</th>
<th>Decontamination Factor</th>
<th>Total Project Capital ($10^6)</th>
<th>Proposed Annual Consumables A ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cryogenic Distillation</td>
<td>67</td>
<td>8.77</td>
<td>267,000A</td>
</tr>
<tr>
<td>MOF Adsorption</td>
<td>100B</td>
<td>8.42</td>
<td>78,000</td>
</tr>
</tbody>
</table>

A: Includes compressor/pump utility loads adjusted to capacity factor and $0.10/kWh, and annual consumables (hydrogen for cryogenic and MOF for the adsorbent process).
B: The MOF DF is theoretical and neither measured nor calculated. The model assumed complete adsorption based on experimental data and performance criteria established in bench scale testing.

- Improve Xe/Kr adsorption at room temperature
- Selectivity

Cabe, J and Thallapally et. al., 2013
Impregnation of silver nanoparticles in Nidobdc

Thallapally et. al., Chem. Commun., 2013
Elemental mapping of Ag@Nidobdc

a) SEM image NiDOBDC; b) Ni; c) O; d) Ag
Powder X-ray Diffraction of Ag@NiDOBDC

Peak @ 39° represent the presence of Ag⁰
Ag@NiDOBdc X-ray photoelectron spectroscopy

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Ag loading (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/DOBDC</td>
<td>781.5</td>
<td>0</td>
</tr>
<tr>
<td>Ni/DOBDC-0005</td>
<td>749.7</td>
<td>1.47</td>
</tr>
<tr>
<td>Ni/DOBDC-001</td>
<td>463.9</td>
<td>1.92</td>
</tr>
<tr>
<td>Ni/DOBDC-01</td>
<td>269.9</td>
<td>6.59</td>
</tr>
</tbody>
</table>
Surface area of Ag@Nidobdc

- Ni/DOBDC ($S_{BET}=781.5 \text{ m}^2/\text{g}$)
- Ag@Ni/DOBDC_00053 ($S_{BET}=749.6 \text{ m}^2/\text{g}$)
- Ag@Ni/DOBDC_001 ($S_{BET}=463.9 \text{ m}^2/\text{g}$)
- Ag@Ni/DOBDC_01 ($S_{BET}=269.8 \text{ m}^2/\text{g}$)
Xe/Kr adsorption in Ag@Nidobdc

![Graph showing Xe/Kr adsorption in Ag@Nidobdc](image)

- **Ag-Ni/DOBDC_Kr**
- **Ag-Ni/DOBDC_Xe**
- **Ni/DOBDC_Kr**
- **Ni/DOBDC_Xe**

**Uptake (wt%)**

**P (mbar)**

15.6%wt
Types of MOFs studied

1. MOF-5, a proto-type
2. MOFs containing open metal sites
3. MOFs functionalized with polar groups
4. MOFs impregnated with Ag\(^0\) nano particles
5. Hydrophobic MOFs with small pore size
6. Computational approach

- Synthesis and Characterization
- Gas sorption properties at 1 bar and various temperatures
- Breakthrough measurements
- Economic analysis

Thallapally et. al., Chem. Comm., 2012, 48, 347
Thallapally et. al., JACS 2012
Thallapally et. al., Chem. Comm., 2012, 48, 347

Thallapally, Cooper et. al., Nature Materials., 13, 954, 2014
Material discovery using computational approach

Modelling predicts the SBMOF-1 is the best among 5000 experimental and 125,000 hypothetical MOFs.

Bernard Smith et. al., Chem. Mat., 2015
Thallapally et. al., Nature Communication, 2016

In Collaboration with Prof. Berend Smit @ University of Berkeley, CA
Leading MOF material @ RT?

- 3D network structure connected with CaO units
- Pore diameter is about 4.1 Angstroms.

![Chemical structure and diagram](image)

**SBMOF-1**

As-synthesized SBMOF-1

Simulated SBMOF-1

![Graphs and data](image)

Surface area - 120 m²/g

120 m²/g

Thallapally et. al., *Nature Communication, 2016*
As synthesized

- No weight loss or decomposition until 500°C, indicating the robustness
- Activated at 290°C

Thermal analysis and gas adsorption

Thallapally et al., Nature Communication, 2016
A rare example of computationally inspired material discovery

- Based on SXRD, it is evident that –phenyl rings turned by 45° to each other as a result blocks the pore when activated at 290 C.
- Due to the ring rotation, the pore size in SBMOF-1 activated at 290 C is less than optimal for Xe atom to fit.
- At lower pressure (~30 mbar) Xe loading is dramatic, 2.5 times more Xe uptake capacity in sample activated at low temperature.

Thallapally et. al., Nature Communication, 2016
Other gas ads in SBMOF-1

✓ SBMOF-1 is very selective towards Xe compare to other gases

Thallapally et. al., Nature Communication, 2016
Breakthrough measurements apparatus

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressed Pressure</td>
<td>75 MPa</td>
</tr>
<tr>
<td>Size</td>
<td>500 – 850</td>
</tr>
<tr>
<td>BET Surface area</td>
<td>15 m²/g</td>
</tr>
<tr>
<td>BET Surface area, Po</td>
<td>120 m²/g</td>
</tr>
</tbody>
</table>

- Identical PXRD confirmed (powder to pellet)
- No amorphous phase
- Reduced BET surface area

Thallapally et. al., Nature Communications, 2016
Single column breakthrough experiments on SBMOF-1 at room temperature

• Conditions
  – Air = 78% N₂, 21% O₂, 0.9% Ar, 0.03% CO₂, 400 ppm Xe, 40 ppm Kr
  – Flow rate = 20 cm³/min
  – T = 25 °C (298K)
  – MOF = SBMOF-1

• Results
  – SBMOF-1 adsorbs Xenon preferentially over other gases
  – Xe capacity = 15 mmol/kg vs 4.6 mmol/kg (NiMOF) and 11 mmol/kg (CC3)
  – >95% of the Xe captured from air
  – Xe/Kr (selectivity) = 15
  – Xe loading is unaffected by water (48% RH)

Thallapally et. al., Nature Communication, 2016
Single column breakthrough experiments with 40% RH

• Conditions
  – Air = 78% N₂, 21% O₂, 0.9% Ar, 0.03% CO₂, 400 ppm Xe, 40 ppm Kr with 40% RH
  – Flow rate = 20 cm³/min
  – T = 25 °C (298K)
  – MOF = SBMOF-1

• Results
  – SBMOF-1 adsorbs Xenon preferentially over other gases
    – Xe capacity = 14 mmol/kg
    – >99% of the Xe captured from air
    – Xe/Kr (selectivity) = 15
    – Xe loading is unaffected by water (48% RH)
Two bed approach to capture Kr
Selectivity of CaDSB or SBMOF-1

The breakthrough capacity is given by

$$q = \frac{C_{vt} \times 10^6}{M_{Tg}}$$

where $C_{vt}$ is the concentration of the gas, $M_T$ is the molecular weight of the gas, and $q$ is the capacity in mmol/kg.

Selectivity of Gas A over B

$$S_{AB} = \frac{x_A/y_A}{x_B/y_B}$$

$x_A$ and $x_B$ are the mole fractions of gases A and B in the adsorbed phase, and $y_A$ and $y_B$ are the mole fractions of gases A and B in the bulk phase.

**Table 2.** Co-adsorption of various gases calculated at the breakthrough point from a column containing CaSDB at room temperature. The capacity and selectivity were calculated from 20 ml/min data.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Breakthrough Time (min)</th>
<th>Capacity (mmol/kg)</th>
<th>Selectivity of Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe</td>
<td>18</td>
<td>16 (33.8)$^a$</td>
<td>14</td>
</tr>
<tr>
<td>Kr</td>
<td>1</td>
<td>0.11 (0.75)$^a$</td>
<td>3</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>5</td>
<td>1.2</td>
<td>209</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.08</td>
<td>47</td>
<td>210</td>
</tr>
<tr>
<td>Ar</td>
<td>0.08</td>
<td>5.28</td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.08</td>
<td>12</td>
<td>206</td>
</tr>
</tbody>
</table>

$^a$ Capacity at equilibrium

**Table 4.** Co-adsorption of various gases calculated at the breakthrough point from single column breakthrough experiments containing CaSDB at room temperature with a gas mixture consisting of 130 ppm Kr, 78.2% N$_2$, 21% O$_2$, 0.9% Ar, and 300 ppm CO$_2$ with a flow rate of 10 ml/min.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Breakthrough Time (min)</th>
<th>Capacity (mmol/kg)</th>
<th>Selectivity of Kr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr</td>
<td>2.5</td>
<td>0.13</td>
<td>0.3</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>7.5</td>
<td>0.90</td>
<td>9.9</td>
</tr>
<tr>
<td>N$_2$</td>
<td>0.25</td>
<td>80.8</td>
<td>9.9</td>
</tr>
<tr>
<td>Ar</td>
<td>0.25</td>
<td>9.09</td>
<td>9.3</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.25</td>
<td>21.2</td>
<td>9.3</td>
</tr>
</tbody>
</table>
Kinetics and cycle experiments

- Faster kinetics, 80% of Xe adsorbed within 10 minutes
- Cycling study indicate no loss of capacity even after 20 cycles.
Identifying Xe and Kr adsorption sites

- SBMOF-1 falls in the optimal pore size and shape for Xe/Kr separations, making it stand out among other MOFs.

Thallapally et. al., Nature Communication, 2016
CaSDB MOF vs other MOFs

SBMOF-1 is best among all other MOFs that PNNL tested at RT and nuclear re-processing condition.

The capacity and selectivity, might be different at low temperature.

Thallapally et. al., Nature Communications, 2016
In conclusion

• The high capacity, selectivity and stability of MOFs allows for applications in
  - nuclear fuel reprocessing
  - pre-concentrators for sensors

• Structure - Property Relationship studies combining modeling, synthesis, testing allows for a feedback loop in the design, tuning and optimization of materials

• Preferential Xe/Kr sorption from Air

• Separation of Xe and Kr in two steps as oppose to multi column distillation

• Economic Analysis suggest: RT separation of Xe/Kr is more economical than cryo-separation.

Thallapally et. al., Nature Communications, 2016
Questions???
Upcoming Webinars

- Iodine-129 (gaseous fission products—capture and immobilization)
- Cesium
- C-14

NAMP website http://www.wipp.energy.gov/namp