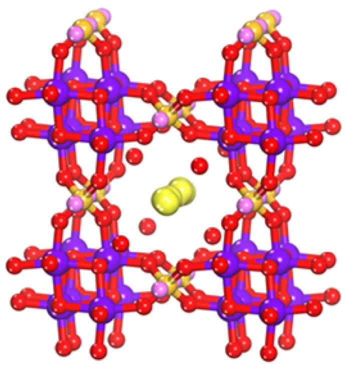
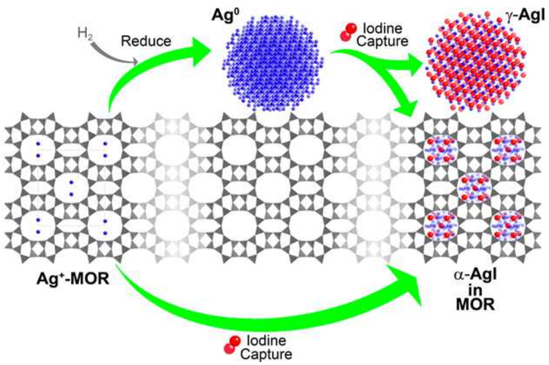
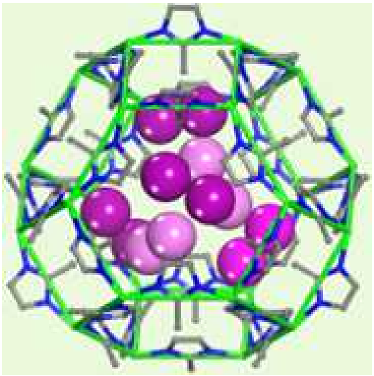
SAND2017-4266D







Sandia's R&D Activity for the Separation & Sequestration of Radiological Materials

Tina M. Nenoff

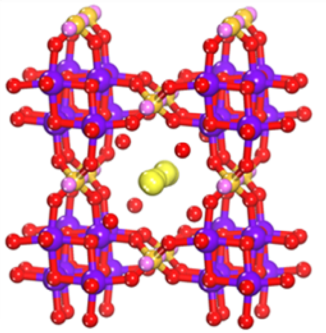
Nanoscale Sciences Department, Sandia National Laboratories

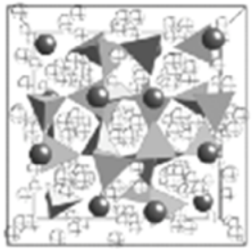
U.S. DEPARTMENT OF ENERGY | Nuclear Energy

NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-mission laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

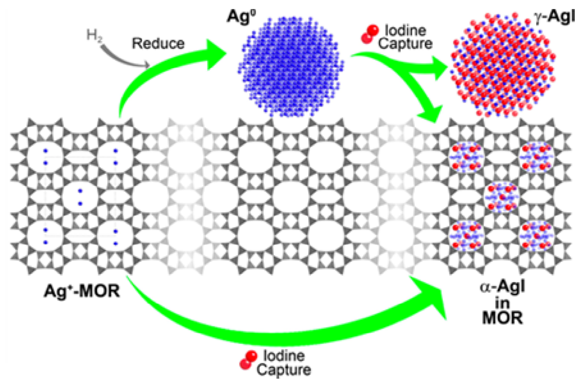
Sandia has Developed Numerous Novel Separations and Waste Form Technologies for DOE/NE Waste Legacy Needs





CST, Cs^+ removal from water to Pollucite Waste Form

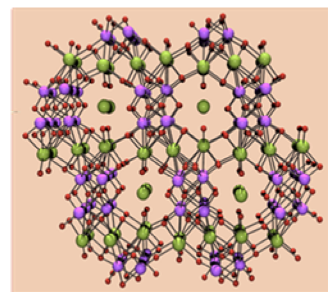
R&D100 1996
JACerS, 2009, 92(9), 2144
JACerS, 2011, 94(9), 3053
Solvent Extr. & Ion Exch, **2012**, *30*, 33

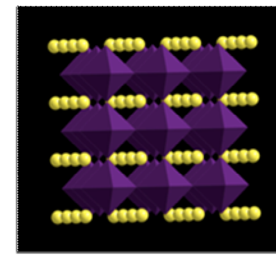


Ag-MOR $I_2(g)$ capture & mechanisms

JACS, **2010**, *132(26)*, 8897
J Phys Chem Letters, **2011**, 2, 2742

Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form

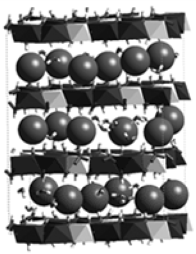


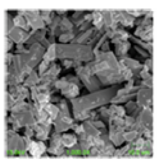


Sr^{2+} getter, 1-step to Perovksite waste form

JACS, **2002**, *124(3)*, 1704

Applied Geochem, **2011**, *26*, 57

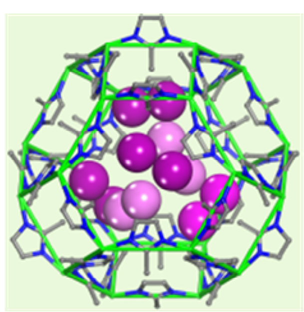


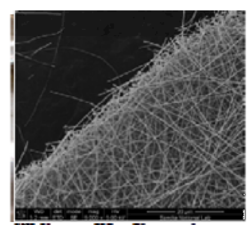


In-situ Iodine removal from water

I_2/MOF, Isolation to Waste Form

JACS, **2011**, *133(32)*, 12398
Ind.Eng.Chem.Res, **2012**, *51(2)*, 614
US Patent 8,262,950; 2012

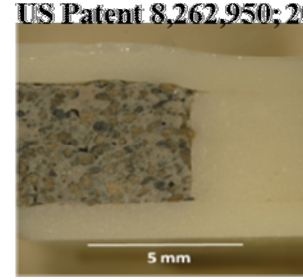




Nanoporous Nanofibers Volatile Gas Removal

US Patent Application, 2011

US Patent 8,262,950; 2012



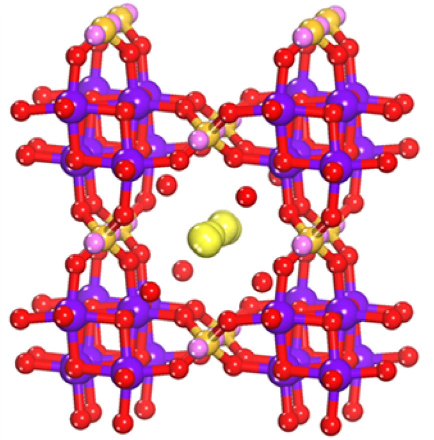
Universal Core-Shell Glass Waste Form Iodine & Getter

JACerS, **2011**, *94(8)*, 2412

Impact Example: Removal of rad-Cs+ from Pooled Seawater at Fukushima Daiichi

Crystalline Silicotitanates (CSTs)
Commercialized for defense legacy waste, applied to reactor accident cleanup
With exceptional Cs^+ selectivity, and mechanical, thermal and radiological stability

Nenoff, SAND96-2578



CST properties:

- Removes 1 part Cs per 100,000 parts Na
- Stable over entire pH range
- Stable in extreme environments
- **1996 R&D 100 Award Winner**

SNL/TAMU US Patents:
6,479,427 (2000) and 6,110,378 (2002)

UOP IONSIV™ IE-911

Five Years, Concept to Commercialization:
Research (1993): Sandia LDRD project – gram reactors
Development: DOE/EM – 1-5 gallon reactors
Commercialization: CRADA with UOP Corp., *IONSIV™ IE-910 & IE-911* (Dec 1995)
1800 lb lots produced

History of CST at Sandia & Fukushima Daiichi Impact

- **2011 (March 11) Earthquake and Tsunami off coast of Japan, Fukushima Daiichi Nuclear Reactor Incident begins**

- **2011 (March 30) Tina Nenoff receives two calls (DOE/NE-SWG & DOE/NE-HQ (J. Kelly and D. Powers)) to study CST use in Cs^+ removal from pooled seawater in Fukushima reactor buildings; David Hobbs (SRS) receives a call from DOE/NE-SWG for Sr^{2+} removal**

- **2011 (April 1) Tina receives p/t for work; invites Jim Krumhansl to team for CST materials testing; discussions with UOP and SNL (Nenoff) begin on availability of IE-911, and general impressions of IONSIV IE-911 effectiveness in seawater from SNL study**

- **2011 (April 8) Tina sends final report to DOE/NE on superior effectiveness of CST (IE-911) over commercial & natural zeolites and clays for Cs^+ removal from concentrated seawater**

- **2011 (April 14) Tina speaks to Bianca Thayer (SNL Tech Transfer office) about UOP and CSTs**

- **2011 (May 16) Initial team conference call between SNL and UOP regarding relicensing options**

- **2011 (August 15) Tina speaks to top UOP zeolite chemists at GRC Nanoporous Materials, and is told : "1- 40K lb batch of IE-911 had been produced and sent to Japan in July 2011"**

- **2011 (October 28) Honeywell UOP signs exclusive relicensing agreement with Sandia for CST; $800,000 to SNL**

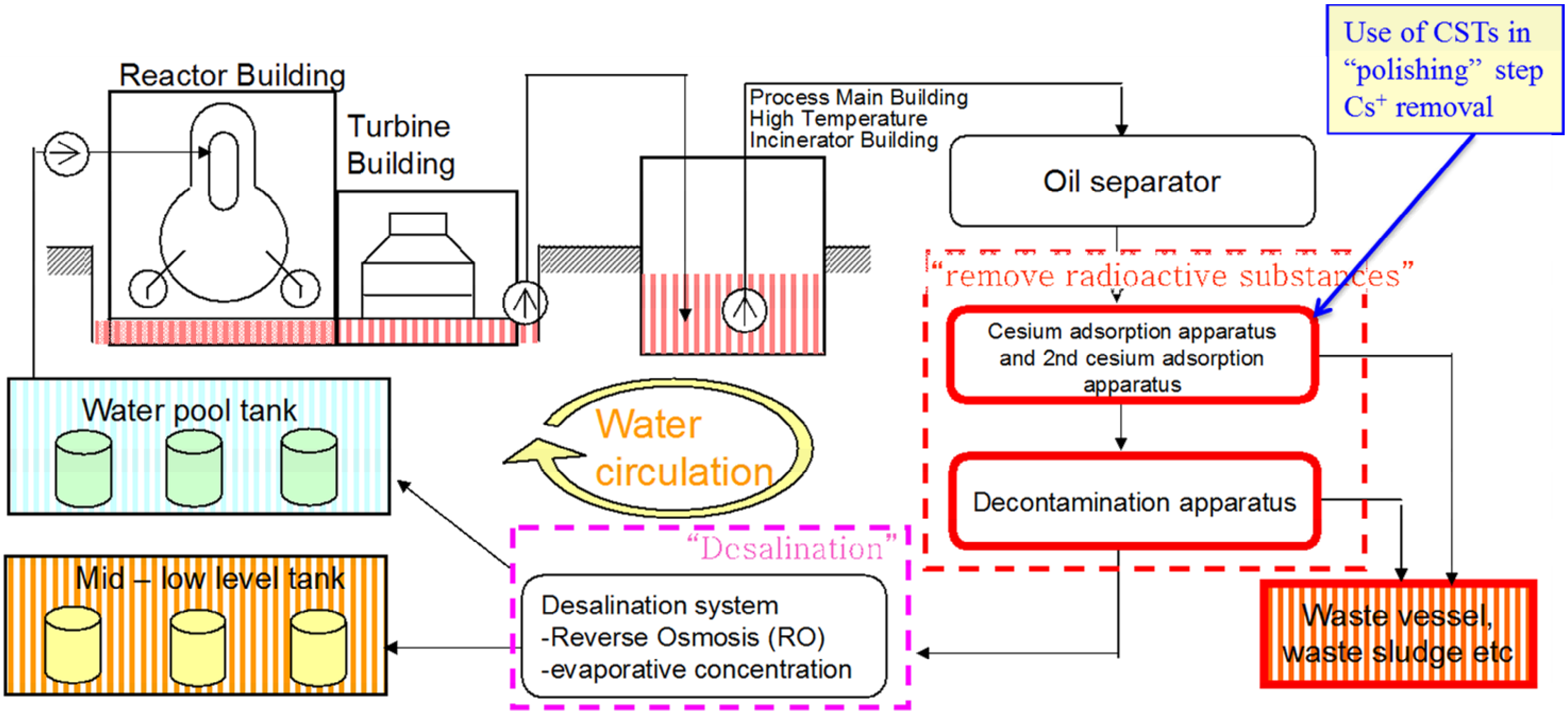
- **2011 (December 8) Honeywell UOP press release: CSTs use in SARRY Process at Fukushima Daiichi**

- **2011- 2012 CRADA discussions underway for further development of CSTs**

- **2012 General Study published; Nenoff, Krumhansl, *Solvent Extraction & Ion Exchange*, 2012, *30*, 33-40**

Water Processing at Fukushima Daiichi, provided by TEPCO

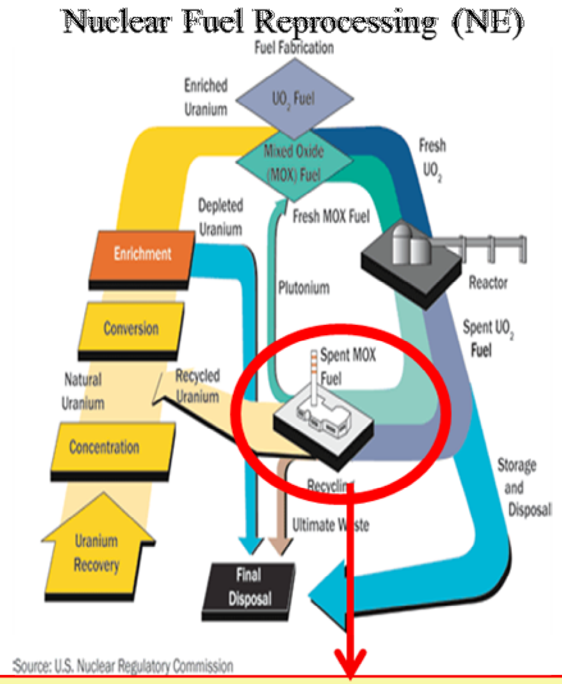
SARRY: Simplified Active Water Retrieve and Recovery System (SARRY)

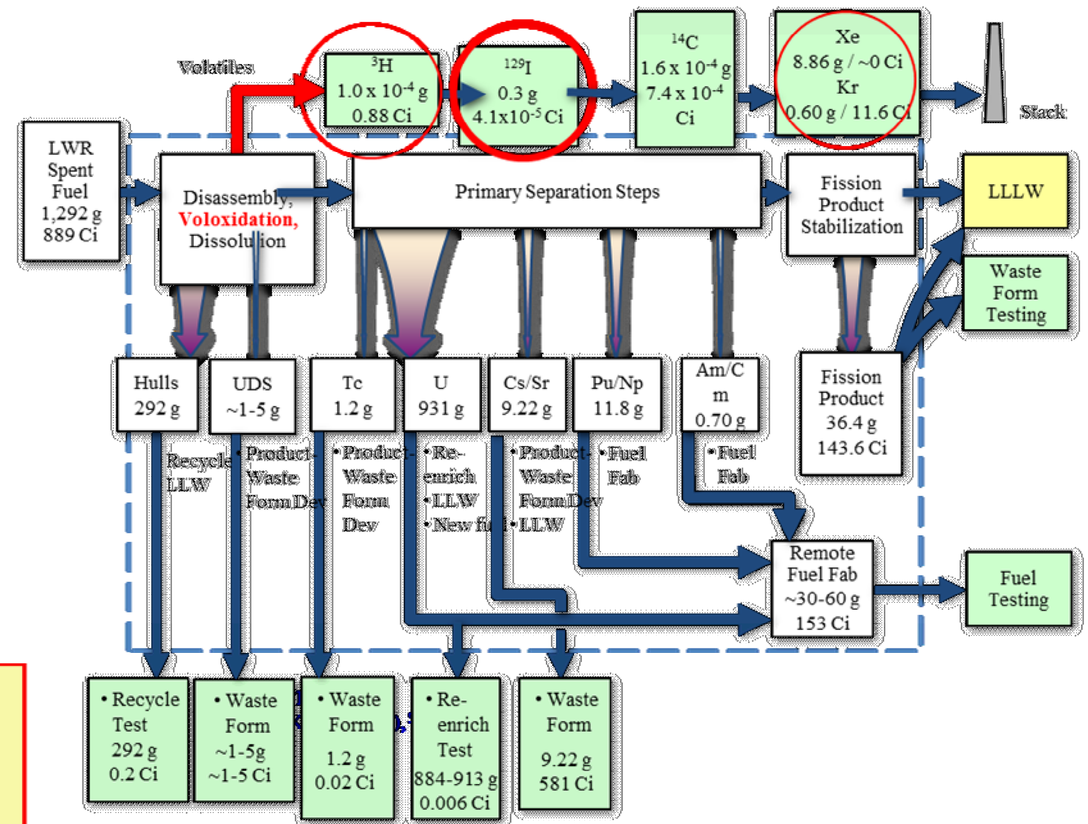


SARRY developed by Toshiba, Shaw Global Services, AVANTech, IHI Corp.

As of December 2014, 160+ million gallons of Cs contaminated seawater has been cleaned with the SARRY Process. The DECON process is ongoing.

Sandia's Role: The Capture & Storage of Volatile Fission Gas Products from Reprocessing and/or Accidents





Separations of non-burnable volatile fission products and lesser actinides

Fundamental materials studies into
- Why known materials work well, and
- Synthesis and Development of new and improved separations materials

Utilizing state-of-the-art
- Predictive modeling
- Synthesis methods
- Characterization methods
- On-line testing in complex streams

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

Provided by R. Jubin, ORNL

^{129}I 1.7 x 10^{7} y
^{131}I 8.04 d

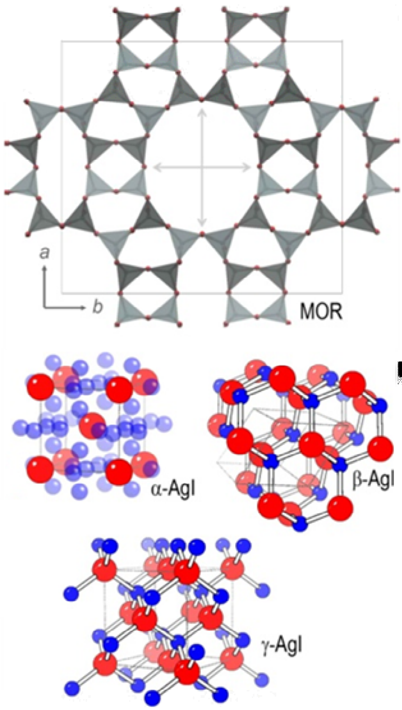
^{90}Sr 29 y
^{81}Kr 2.1 x 10^{5} y
^{133}Xe days

T. M. Nenoff, tmnenof@sandia.gov

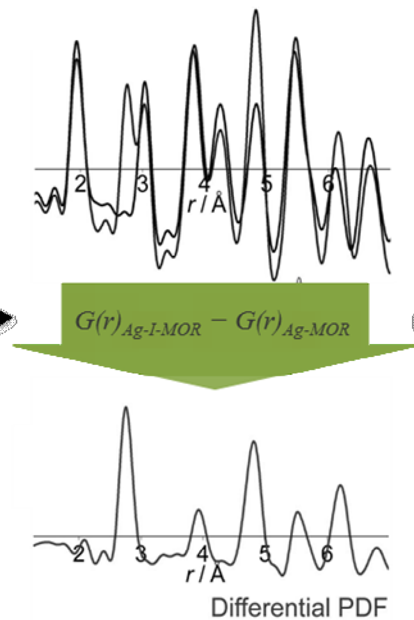
Understanding the Mechanism of I_2 Capture in Implemented Ag-Mordenite Baseline Materials

U.S. DEPARTMENT OF ENERGY Nuclear Energy | Sandia National Laboratories

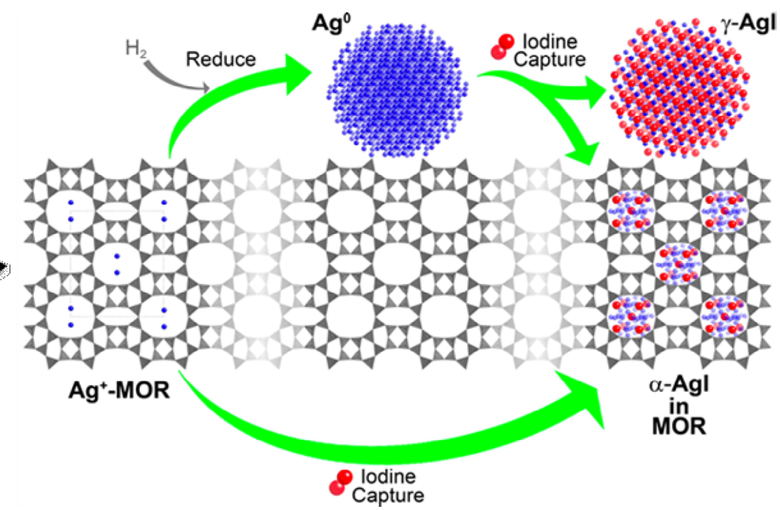
Use of SNL materials for study at ANL synchrotron: Allows for determining short range guest interactions (eg., AgI) within porous materials



Components



Synchrotron Studies of Zeolite and AgI in pores



Mechanism of AgI formation & phase determination

Impact: Improved Materials Understanding of the Capture Mechanisms for improving Waste Form Performance

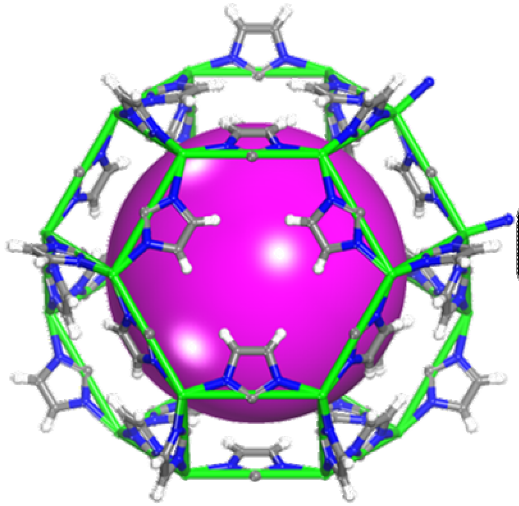
Nenoff, et.al., *JACS*, **2010**, *132*(26), 8897

What's after Zeolites? Metal Organic Frameworks (MOFs) for Radiological Gas Sorption

U.S. DEPARTMENT OF ENERGY Nuclear Energy | Sandia National Laboratories

Traditionally zeolites/molecular sieves are used as baseline materials for selectivity and sorption. Cutting edge materials are tuned for high selectivity and high capacity.

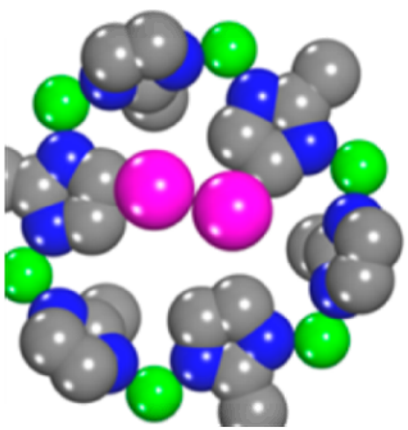
Basolite Z1200, ZIF-8
Constricted Pore Opening (≈ 3.4Å)
1100 – 1600 m^2/g
Pore Volume = 0.636 cc/g
stable in Air & H_2O

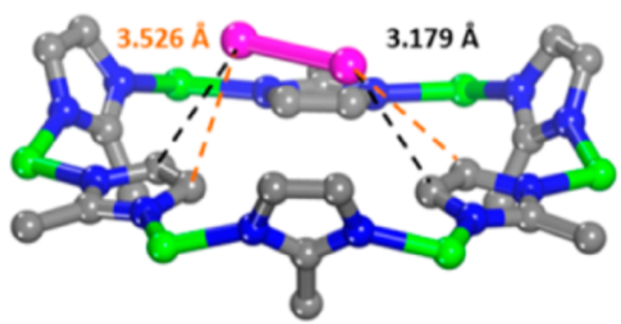


I_2@ZIF-8 ~ 125 wt.% I_2

JACS, **2011**, *133*(32),12398

Opportunity: R&D of MOFs for next generation radiological sorption needs.



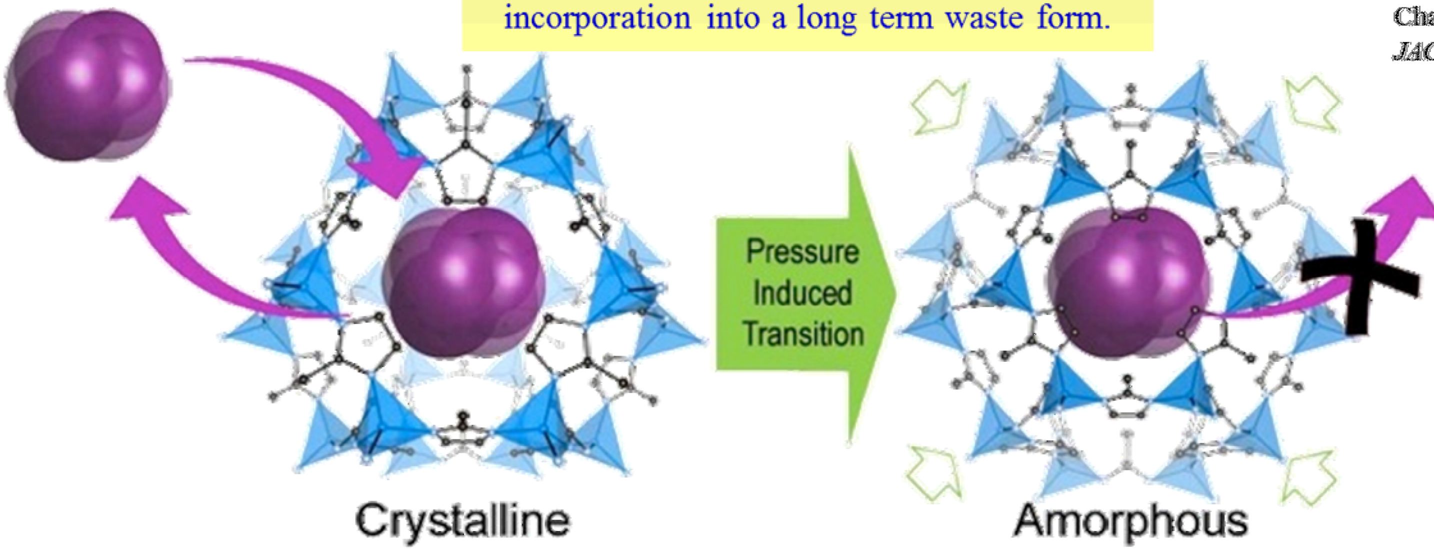


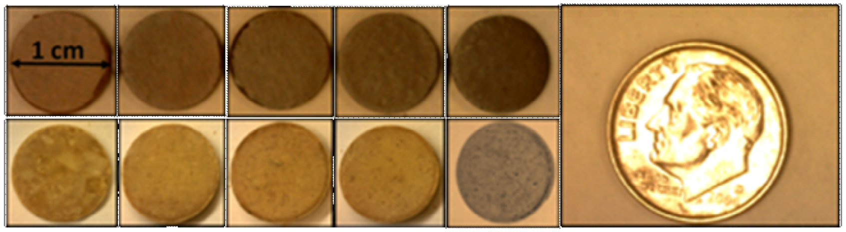
JACS **2013**, 135, 16256

I_2@ZIF-8 Pressure-Induced Amorphization of Trapped Gases: Enhanced Retention

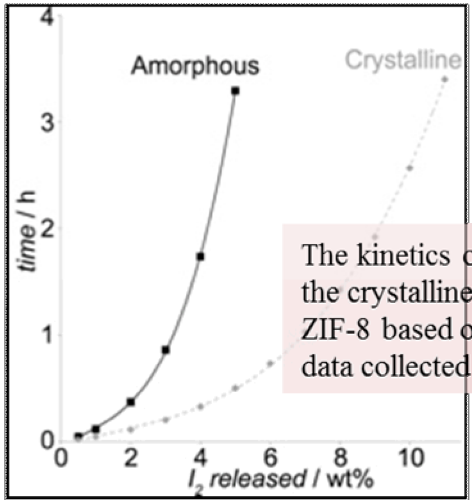
Secure consolidated interim storage before incorporation into a long term waste form.

Chapman, Nenoff, et.al., *JACS* **2011**, *133*(46), 18583.





Crack free pellets of iodine loaded ZIF-8 powders were obtained by applying uniaxial mechanical pressure.



The kinetics of I_2 release from the crystalline and amorphized ZIF-8 based on isothermal TGA data collected at 200°C, 4hours

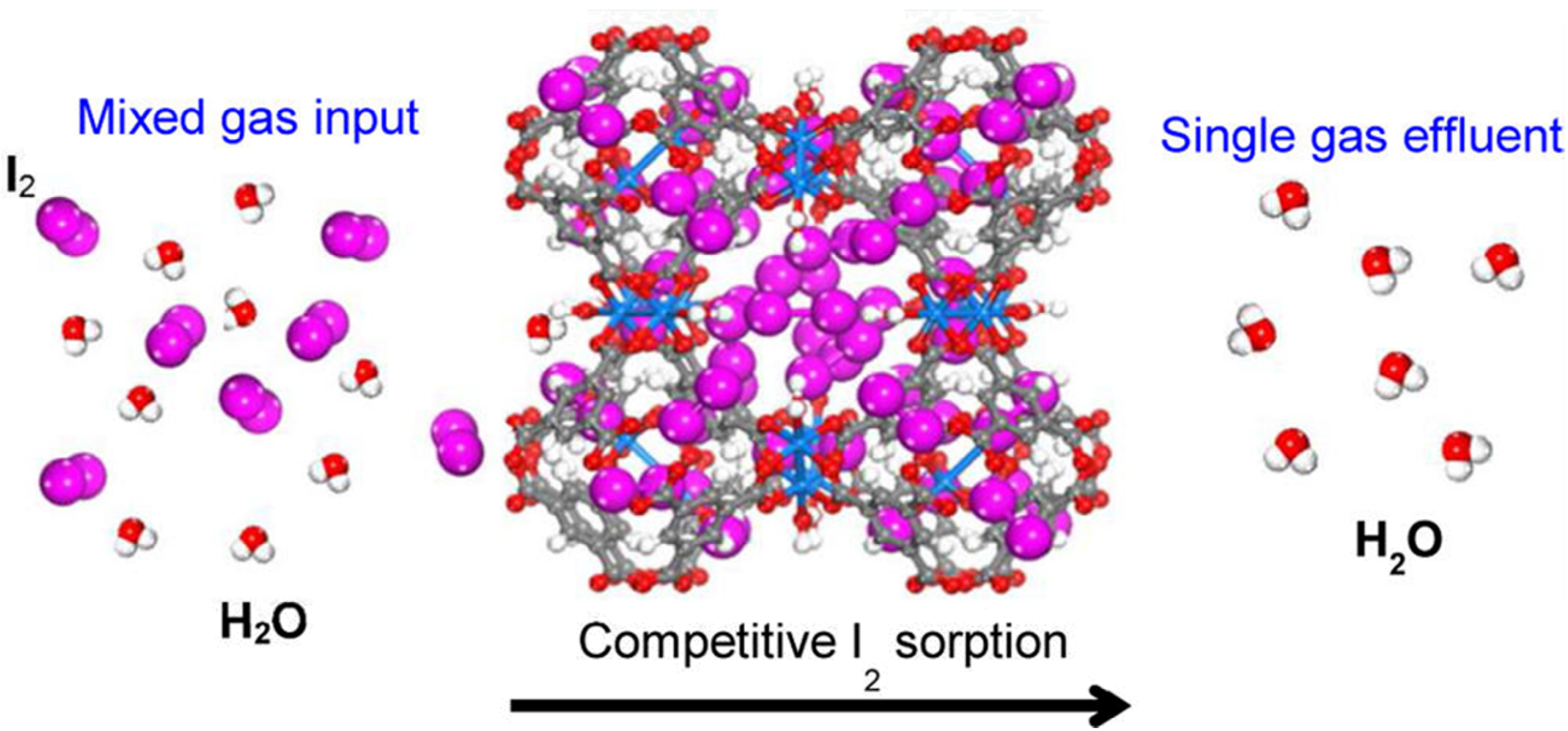
Crystal Structure of I_2@HKUST-1, co-adsorption of I_2 and H_2O

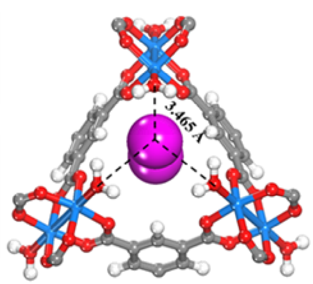
U.S. DEPARTMENT OF ENERGY Nuclear Energy

Sandia National Laboratories

I_2/HKUST-1 **3.3 I/Cu**

Sava Gallis, Nenoff, et.al., *Chem. Mater.*, **2013**, *25* (13), 2591

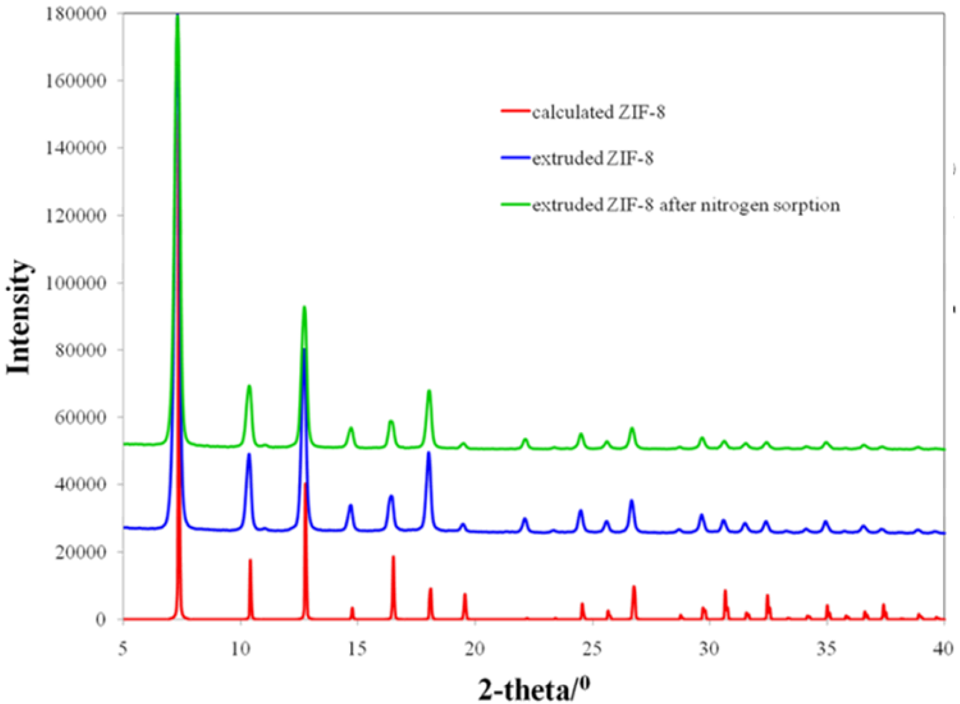


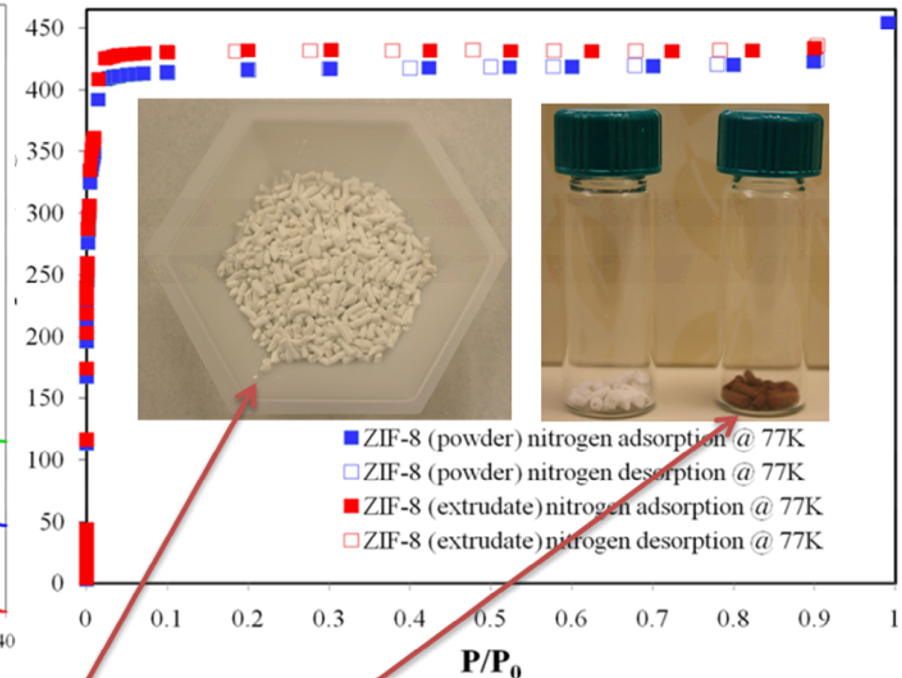


No Evidence of HI; possible combination of physi- and chemi-sorption of I_2
Iodine gas behaves *hydrophilic* in the HKUST-1 framework

Next Steps : Interests toward Scale Up and Commercialization Pathways

US Provisional Patent submitted, 2014





The proposed pelletized form factor would allow for the straightforward adaptation of MOF pellets in existing filtration systems. MOF color change due to iodine absorption.

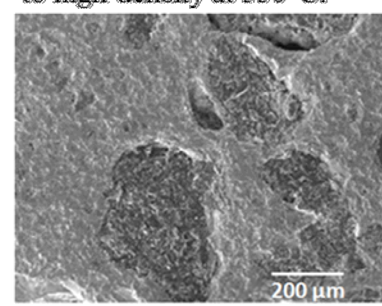
Regularly sized pellets
Maintained surface area of MOF
1850-1900 m^2/g

Sandia's Low-sintering Temperature Glasses For Fission Products (eg., ^{129}I) Waste Encapsulation

- Lower temperature compared to melting is possible since glass powder is densified by sintering. **No HIPping** is required.
- A composite is formed with a dense matrix surrounding I-containing phase.
- Bi-Si-Zn-Al oxide glass - best chemistry and durability.
- **Flexible matrix/ "Universal" Waste Form: Variety of loaded getter materials incorporated and resulting waste form is durable.**

  Eg., AgI/glass, AgI-MOR/glass, Cs-CSTs/glass, I-MOF/glass

Glass/AgI-MOR pellet sintered to high density at 550°C.



Property	Value
Composition	**Bi-Si-Zn-Al oxide**
Sintering Schedule	**550°C for 1 hr**
CTE	**7.8×10^{-6}/°C**
Density	**5.8 g/cm^3**

J. Am. Ceram. Soc., **2011**, *94*(8), 2412-2419
US Patent: 8,262,950, September 11, 2012

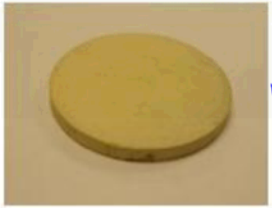
Sandia GCM: "Universal" Waste Form Material

U.S. DEPARTMENT OF ENERGY
Nuclear Energy
Sandia National Laboratories

US Patent 8,262,950; Sept 2012

Homogenous Glass GCM: for
AgI or AgI-MOR off-gas capture and storage

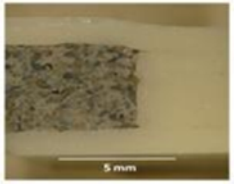
50 wt% AgI/50 wt% Glass
500˚C for 3 hr



50 wt% AgI/50 wt% Glass,
500°C for 3 hr

Core-Shell GCM Glass Waste Forms

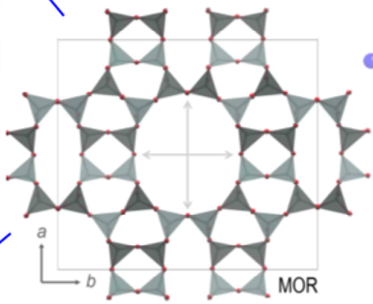
Glass shell, AgI/glass core,
75/25

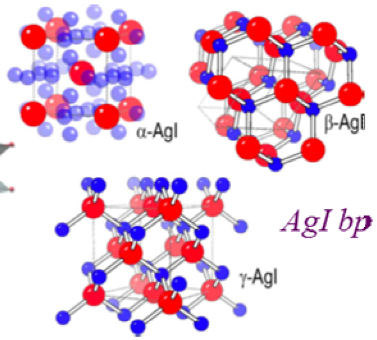


Glass shell,
AgI-MOR/Ag/Glass core 80/20/5

JACerS, **2011**, *94*(8), 2412

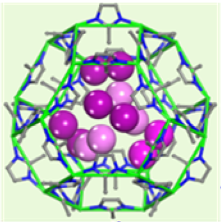
"Universal" Low Temperature Glass Waste Form
Durabilty studies show that SNL GCM can successfully incorporate and store a wide variety of "fission gas – loaded" oxide based *getters*



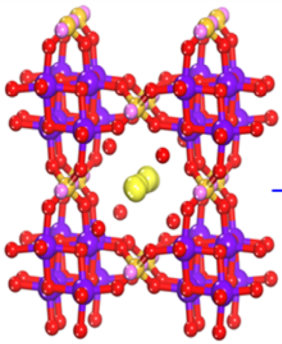


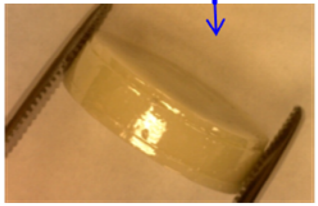
AgI bp ***556˚ C***

I_2/MOF, Isolation to Waste Form
JACS, **2011**, *133*(32), 12398
Ind. Eng. Chem. Res (Invited Article) **2012**, *51*(2), 614



Cs-CST Low Temp Glass Waste Form, No Cs Loss in Sintering





Future Work

SNL materials research: Nanoscale discoveries fed into bulk scale performance.

Tunability for extreme selectivity of Cs^+, Sr^{2+}, fission gases

CSTs in production by Honeywell UOP LLC: Ionsiev IE-910 & IE-911

Determination of mechanisms for iodine species capture (eg., I_2, HI, Org-iodides, etc)

Metal organic Frameworks (MOFs) show high selectivity for I_2 from complex streams and promise for improving next generation waste forms. Efforts are hindered by a lack of sustained long range R&D support.

Waste Forms: SNL produced low temperature sintering Glass Composite Material Waste Form (GCM) with durability ***equal to or better than*** standard nuclear glass waste forms
- incorporates: zeolites, molecular sieves/CSTs, MOFs

In AgI-MOR + Bi-Si-Glass + Ag (AgI-GCM): pH-dependence to the GCM degradation rates suggests that the **glass degradation mechanism is surface driven**

Iodine release is likely controlled by AgI solubility.

SPFT, PCT, and MCC-1 results and analysis indicate that I release from the GCM waste form will be **insensitive to Iodine loading**.