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Nanoporous Materials for Environmental and Energy Applications

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Team Members and Collaborators

Nanoporous/ Ceramic Materials, Analysis:

Dorina F. Sava Gallis, Mark A. Rodriguez, Patrick V. Brady, Terry J. Garino, Lauren E. S. Rohwer, Curtis D. Mowry

Modeling: Marie V. Parkes, Jeffery A. Greathouse, Scott M. Paap

Synchrotron: Karena Chapman, Peter Chupas, APS/ANL

Thermochemistry: Alexandra Navrotsky, UC Davis

Membranes: Junhong Dong, Univ Cincinnati

T. M. Nenoff, tmnenof@sandia.gov

Technical Focus

- Technical Focus:
  Chemical study of confinement and reactivity of ions and molecules in micro- and nano-porous materials
  - zeolites, metal-organic frameworks (MOFs), clays and amorphous silicas

- The study of Structure-Property Relationships on the nanoscale enabling the informed testing of the materials for a wide range of interests.

- Structure analysis of host-guest systems on the nanoscale has led to strong collaborations with staff scientists at the APS for synchrotron data collection & Pair Distribution Function (PDF) analysis

- Strong Interdisciplinary Teams working in concert.
  diverse programs require diverse teams
  chemists, engineers, computational modelers
  national labs, universities and industry

- Mentoring: postdocs, young staff and collaborating young professors,
  strong support of women and minorities into the sciences

Program Development & Management - Nenoff

- Raised \$35+ Million raised in individual PI grants
  150+ publications, 13 US Patents, 4 book chapters, *h*-index = 33

- Developed strong relationships at DOE, resulted in *long running* programs
  - DOE/EERE/Office of Industrial Technologies (Advanced Materials)
  - DOE/EERE/Hydrogen
  - DOE/Environmental Management
  - DOE/Office of Nuclear Energy

Building customers with ARPA-E, DOE/BES, and DOE/Fossil Energy (NETL)

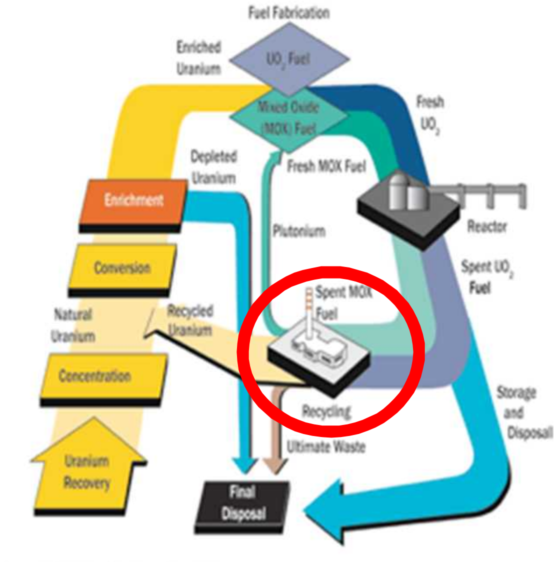
- Research Group works in *TRL 1 - 9*

- Led 2 different multiyear, multimillion \$ CRADAs
  - SNL, BP, Temec, Coors Ceramics, University Cincinnati:
    Zeolite Membranes for HC isomer feedstock purification
  - SNL, Goodyear Chemicals, University Cincinnati:
    Membranes for Separations of High Volume $C_4/C_5/C_6$ Mixtures

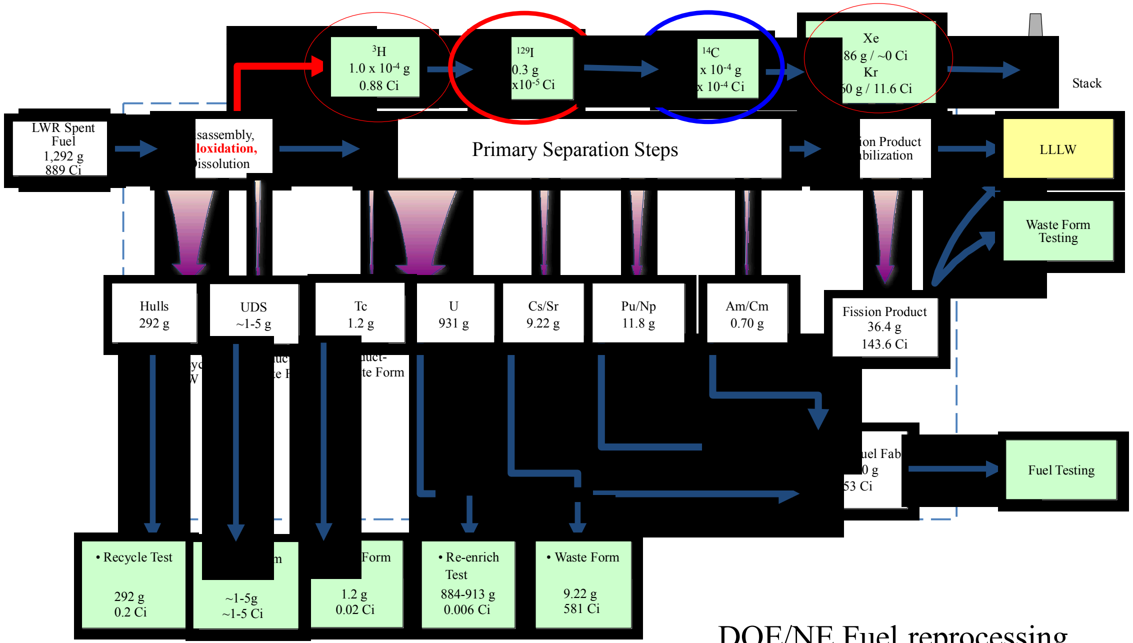
T. M. Nenoff, tmnenof@sandia.gov

Applications

Reprocessing: capture on nonburnable volatile fission products and lesser actinides



Source: U.S. Nuclear Regulatory Commission



DOE/NE Fuel reprocessing Scheme, ORNL

Legacy, Accident or Produced rad aqueous waste requiring highly specific ion capture

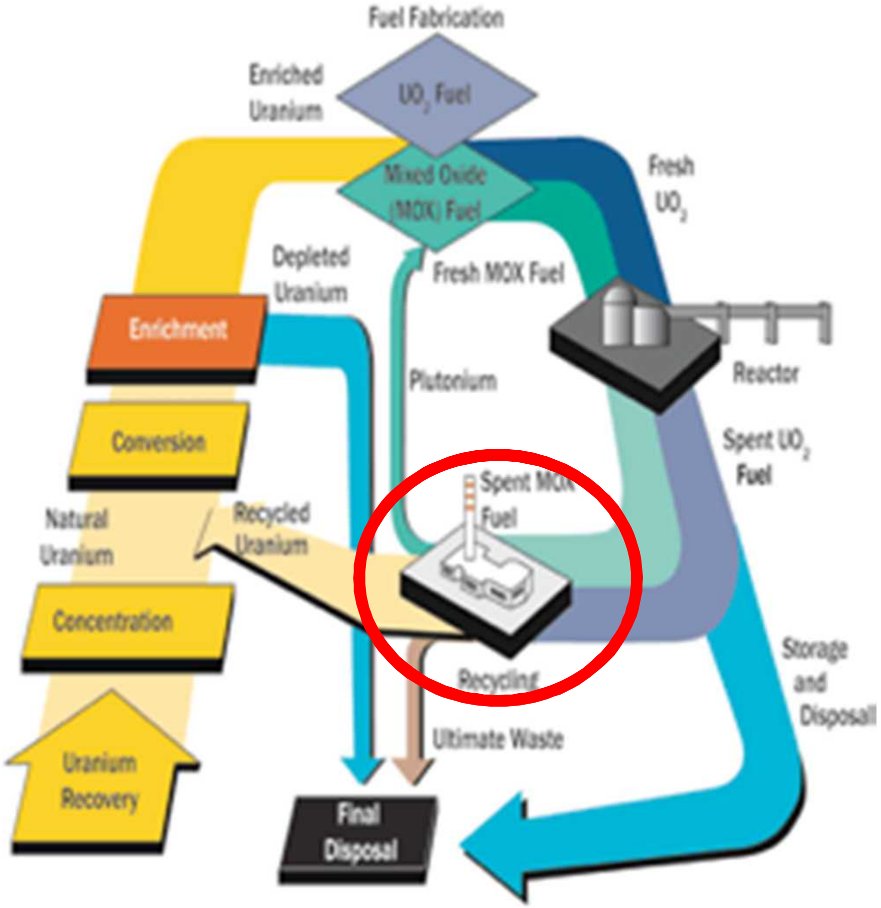
Fukashima Daiichi Nuclear Power Plant explosion 2011
I^{129}, I^{131} volatile gas released;
Cs^{135}, Cs^{137} & Sr^{90} aqueous released
(www.IAEA.org)


Hanford Tank Farm

Elements, Dec 2006

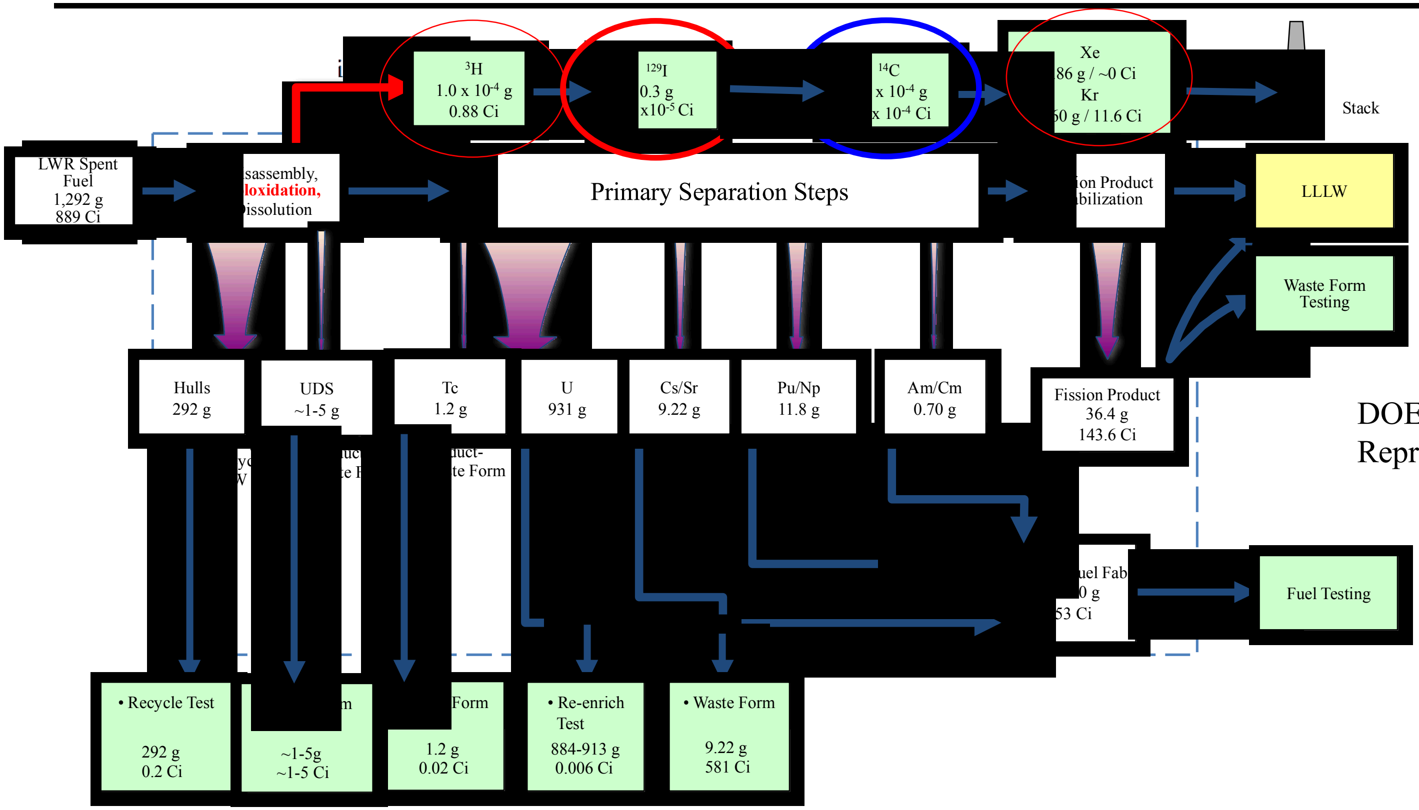
Applications: Fission Gases

Reprocessing: capture on nonburnable volatile fission products and lesser actinides



Source: U.S. Nuclear Regulatory Commission

Applications: Fission Gases



^{3}H
1.0 x 10^{-4} g
0.88 Ci

^{129}I
0.3 g
x10^{-5} Ci

^{14}C
x 10^{-4} g
x 10^{-4} Ci

Xe
86 g / ~0 Ci
Kr
0 g / 11.6 Ci

Stack

LWR Spent Fuel
1,292 g
889 Ci

sassembly,
loxidation,
issolution

Primary Separation Steps

ion Product
bilization

LLLW

Waste Form Testing

Hulls
292 g

UDS
~1-5 g

Tc
1.2 g

U
931 g

Cs/Sr
9.22 g

Pu/Np
11.8 g

Am/Cm
0.70 g

Fission Product
36.4 g
143.6 Ci

uct-
te Form

uel Fab
0 g
53 Ci

Fuel Testing

- Recycle Test

292 g
0.2 Ci

m

~1-5g
~1-5 Ci

Form

1.2 g
0.02 Ci

- Re-enrich Test

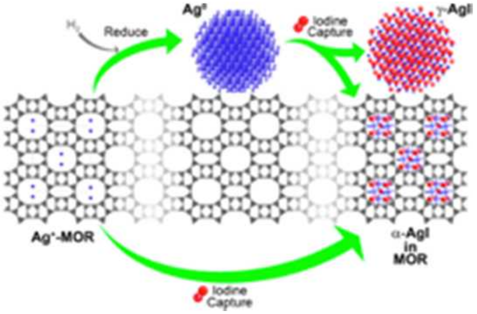
884-913 g
0.006 Ci

- Waste Form

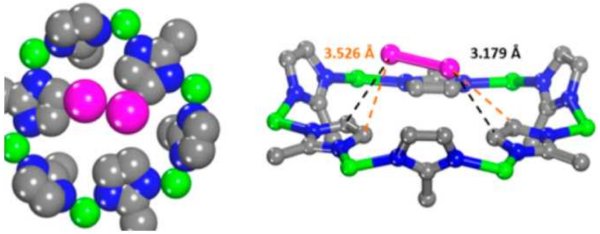
9.22 g
581 Ci

DOE/NE Aqueous Fuel Reprocessing Scheme, ORNL

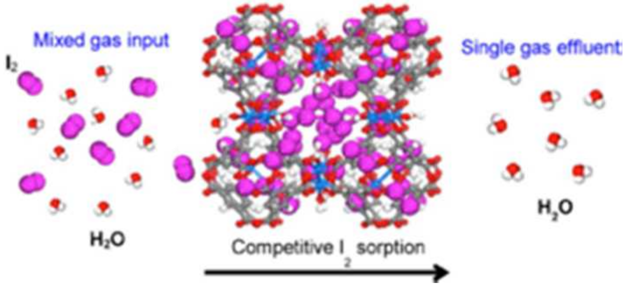
Zeolites – I_2 capture/storage



MOFs – small pore for large quantity I_2 capture



MOFs – large pore for competitive I_2 vs H_2O, and large volumes



Applications: Rad Ion Capture

Legacy, Accident or Produced rad aqueous waste requiring highly specific ion capture.

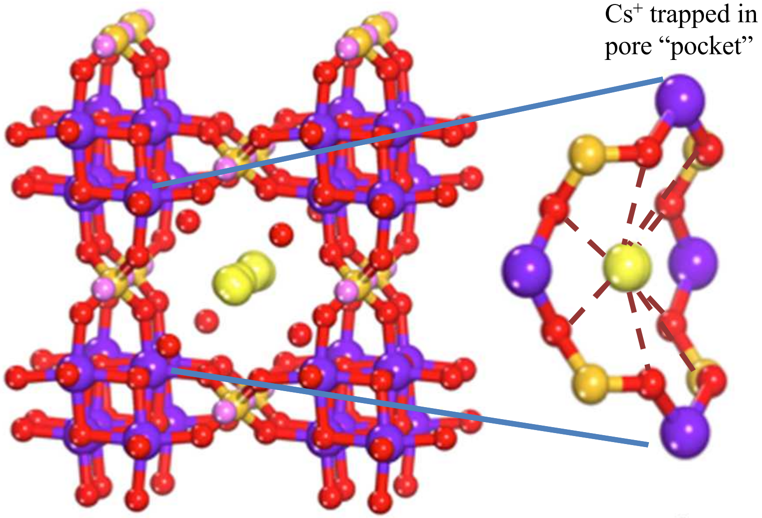
Cs+ ion capture: Crystalline Silicotitanates (CSTs)

Fukashima Daiichi
Nuclear Power
Plant explosion 2011
I^{129}, I^{131} volatile
gas released;
Cs^{135}, Cs^{137} & Sr^{90}
aqueous released
(www.IAEA.org)

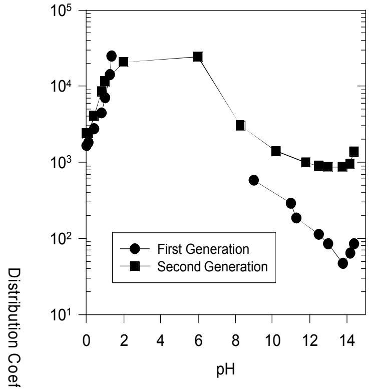

Hanford Tank Farm

Elements, Dec 2006

Cs^+ captured in CST cage


Cs^+ trapped in pore "pocket"

Distribution Coefficient of Cs on CST



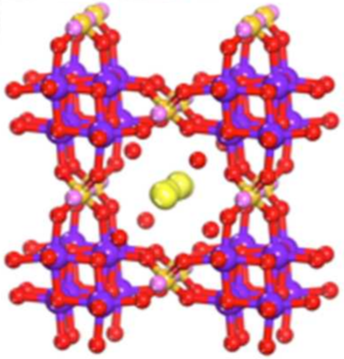
UOP IONSIV^{TM} IE-911:
LDRD idea to Commercial product in 5 years

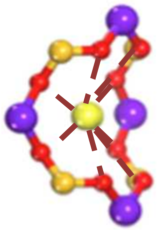
CSTs used in Cs^+ cleanup of 160M+ gallons from seawater in Fukushima buildings

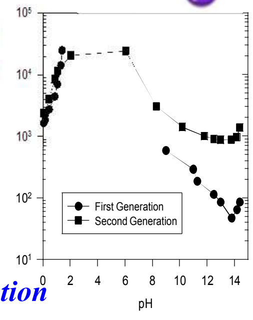
Augmentation of accumulated water processing facility (SARRY)

T. M. Nenoff, tmnenof@sandia.gov

Example 1: Nanoporous Materials (Zeolites, Molecular Sieves & MOFs), Radiological Ion and Gas Capture

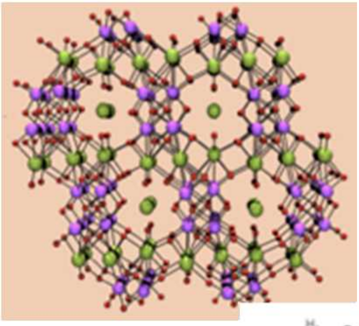






CST, Molecular Sieve:
R&D100 1996
JACerS, 2009, *92(9)*, 2144
JACerS, 2011, *94(9)*, 3053
Solvent Extr. & Ion Exch, 2012, *30*, 33

CST, Cs^+ removal from water to Pollucite Waste Form
US Patents *6,479,427; 6,110,378*

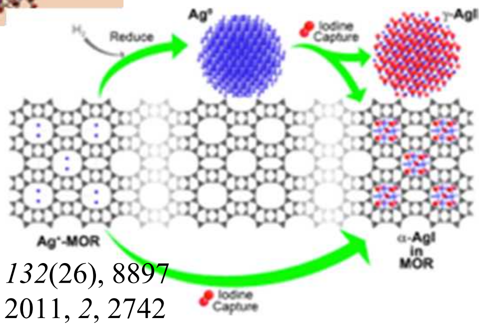


SOMS Molecular Sieve,
Sr^{2+} getter,
1-step to Perovksite WF
JACS, 2002,*124(3)*, 1704
US Patent *7,122,164;* 2006

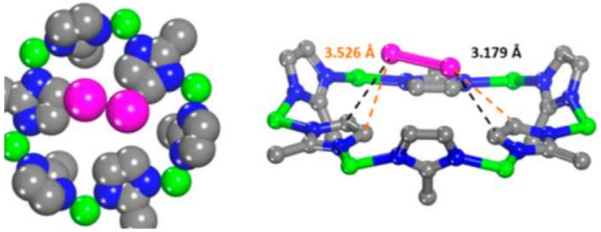
Design, Produce, Test and Commercialize Materials with Specific Selectivity to Ion/Gas by Size & Chemistry of Nanopore

I_2/ZIF-8 MOF, *Encapsulation to Waste Form*
JACS, 2011,*133(32)*,12398
JACS 2013, *135*, 16256

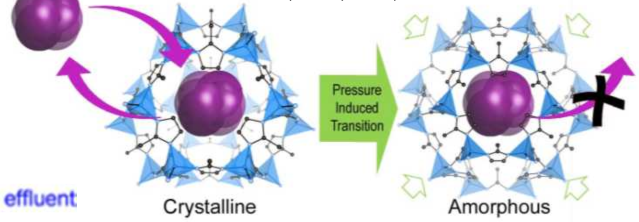
Ag-MOR Zeolite,
$I_2(g)$ capture & mechanisms

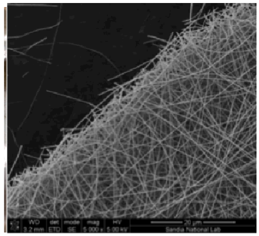


JACS, 2010, *132*(26), 8897
JPC Letters, 2011, *2*, 2742

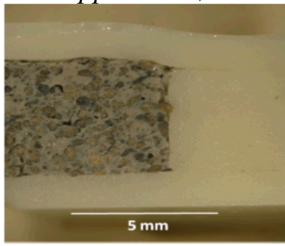


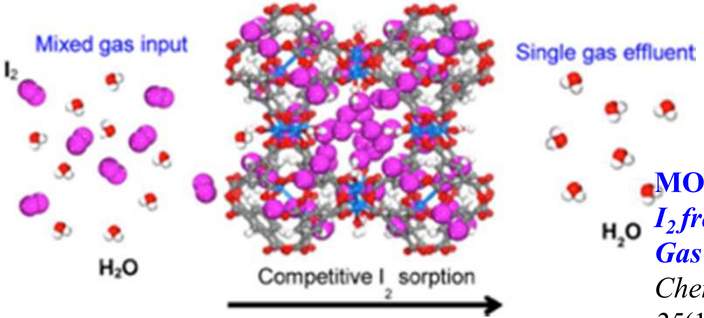
MOF *Amorphization for Gas Storage*
JACS, 2011,*133*(46),18583
US Patent *9,162,914;* 2015



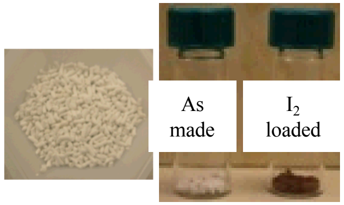


TiO_2 Nanoporous Nanofibers
Volatile Gas Removal
US Patent Application,2011





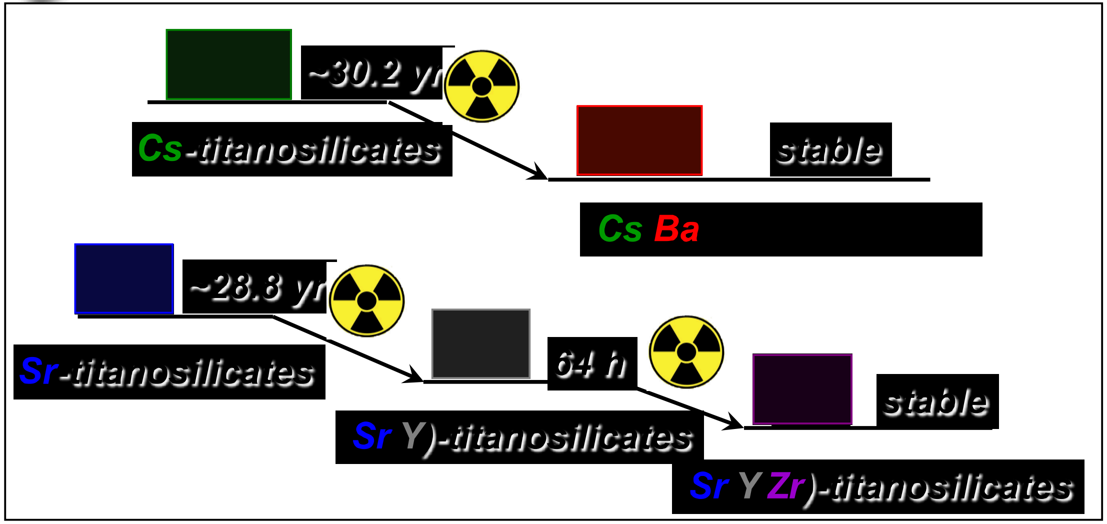
MOF Cu-BTC:
I_2 from Humid Gas Stream
Chem. Mater. 2013, *25*(13), 2591



Binder Free* MOF *Pelletization
US Patent Pending 2014

Glass Composite Material GCM:
Universal Core-Shell Iodine Glass Waste Form & Getter
JACerS, 2011, *94*(8), 2412
US Patent *8,262,950*; 2012

CSTs Waste Form: Pollucite Ceramic Oxide



~30.2 yr

Cs-titanosilicates

stable

Cs Ba

~28.8 yr

Sr-titanosilicates

64 h

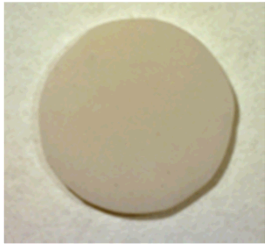
stable

Sr Y)-titanosilicates

Sr Y Zr)-titanosilicates

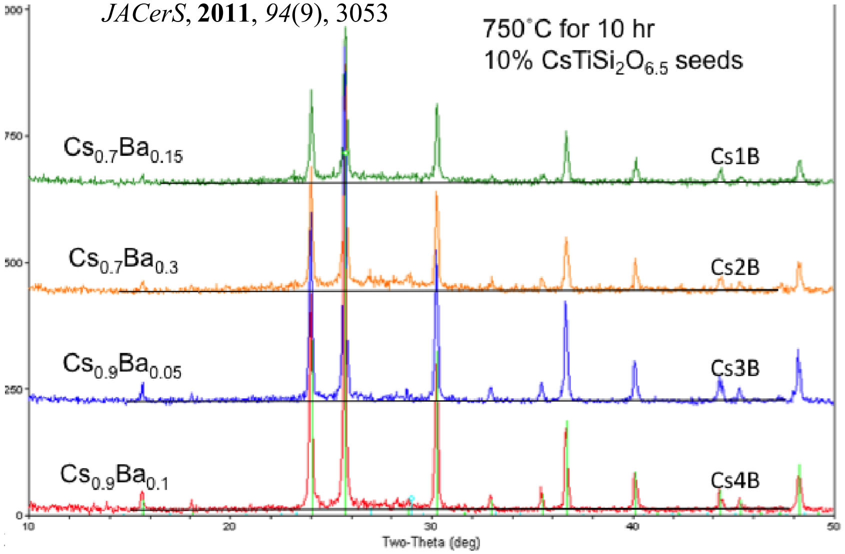
On-going basic research:
into an in-situ Waste Form with framework flexibility to compensate for oxidation state changes with decay

$Cs_{0.9}Ba_{0.05}TiSi_2O_{6.5}$



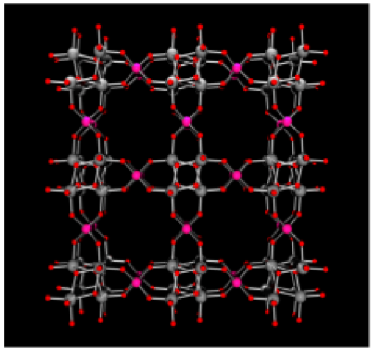
Proof of Ba incorporation

JACerS, **2009**, *92*(9), 2144
JACerS, **2009**, *92*(9), 2053
JACerS, **2011**, *94*(9), 3053



Traditionally: Incorporation into Borosilicate Glass Log
~ 5wt% loading limit, 1200°C heating temp

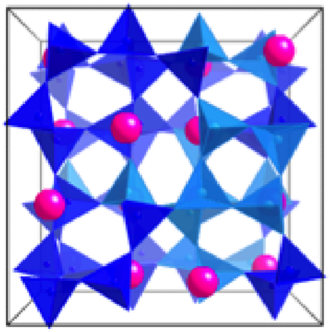
↑



CST: $CsSi_2Ti_4O_{13}$•$4H_2O$

heat →
>700°C

Balmer, et.al., 1997



Pollucite: $CsTiSi_2O_{6.5}$

Waste Forms: New Low Temperature Glass for Rad-occluded Zeolites and MOFs

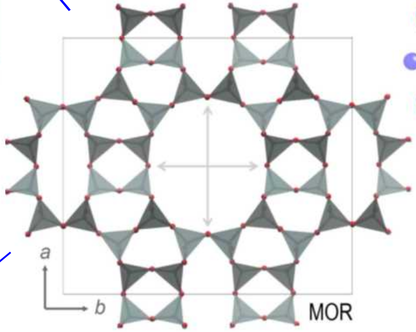
Homogenous Glass GCM: for
AgI or AgI-MOR off-gas capture and storage

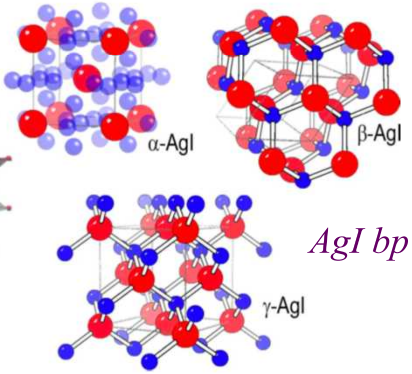
50 wt% AgI/50 wt% Glass
500°C for 3 hr

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

Glass Composition (2922), no HIP-ping needed:
Sintering 550°C, Mole % oxides:
32 BiO$_3$, 19 ZnO, 44 SiO$_2$, 5Al$_2$O$_3$

US Patent 8,262,950; 2012

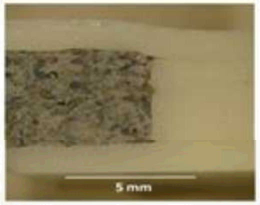




AgI bp 556° C

Core-Shell GCM Glass Waste Forms

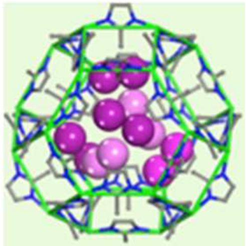
Glass shell, AgI/glass core,
75/25



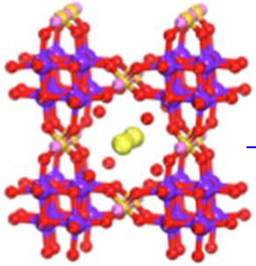
Glass shell,
AgI-MOR/Ag/Glass core 80/20/5

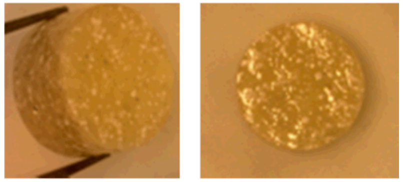
JACerS, **2011**, *94*(8), 2412

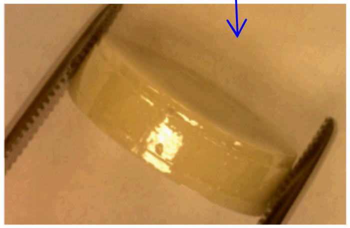
I$_2$/MOF, Isolation
to Waste Form
JACS, **2011**,*133(32),*12398
Ind. Eng. Chem. Res (Invited Article*)*
2012, *51*(2), *614*



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







Materials Aging

Needs of testing on Sandia materials:

- Radiation and decay effects on sorption materials and waste forms
- Durability in high radiation fields
- Durability of waste forms, accelerated aging predictions based in science (SPFT, calorimetry, ion beam)

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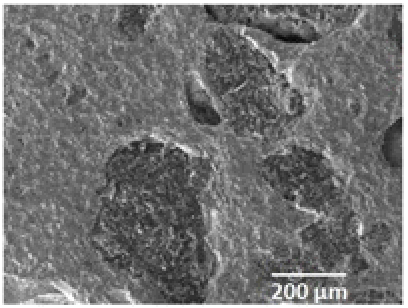
Low-sintering Temperature Glasses for ^{129}I Waste Encapsulation

- 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: Both AgI/glass and AgI-MOR/glass compositions were fabricated.

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

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



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

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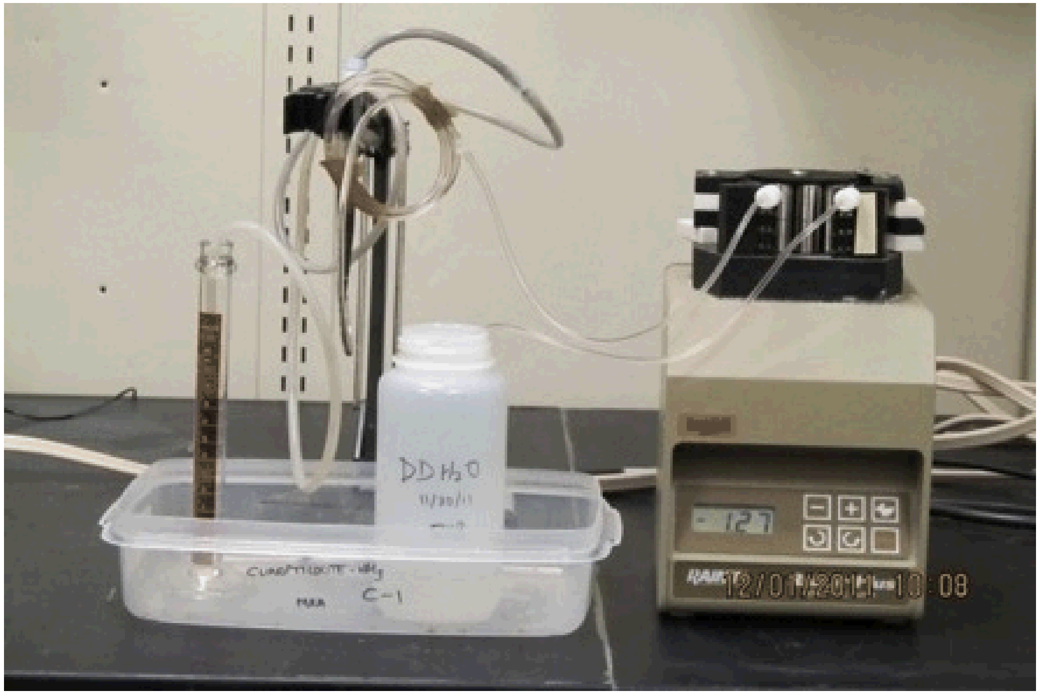
Single Pass Flow Through Test (SPFT) Of Waste Form Material

For SPFT, for AgI-GCM:
Ground to ~ 3 microns (glass)
0.1 - 1 grams in 2 ml vol reactor
Surface area = 2.6 (glass), 21 (AgI-MOR) m^2/g
Temps: 25 and 60°C
pH: 3.3 – 7.5
Test solutions pumped:
220 – 340 ml/day ($2.5 – 3.9 \times 10^{-7}$ L/s)

Upflow Configuration; water-jacketed and thermostatted for high temperature runs.



Elemental release rates were calculated as: **Rate (mol/cm^2s) = DC_iP/SAf**

DC_i is the molarity of the i'th component measured in the effluent;
P is the pumping rate(L/s); and SA is the material surface area (cm^2); and
f is the mass fraction of Si in the Bi-Si glass (0.234) or AgI-Mordenite (0.3).

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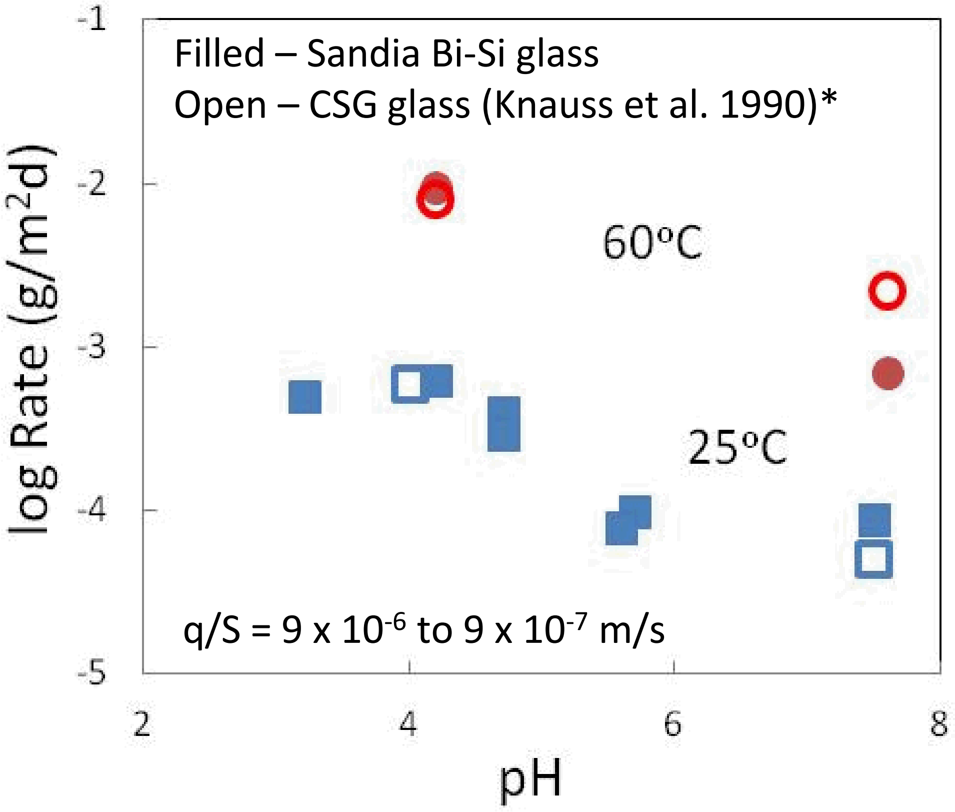
Measure effect of pH and temperature on Bi-Si glass dissolution

Steady-state Bi-Si and CSG Glass Degradation Rates



*Knauss, K.G.; Bourcier, W.L.; McKeegan, K.D.; Merzbacher, C.I.; Nguyen, S.N.; Ryerson, F.J.; Smith, D.K.; Weed, H.C.; and Newton, L. 1990. “Dissolution Kinetics of a Simple Analogue Nuclear Waste Glass as a Function of pH, Time and Temperature.” *Scientific Basis for Nuclear Waste Management XIII, Symposium held November 27-30, 1989, Boston, Massachusetts*. Oversby, V.M. and Brown, P.W., eds. 176, 371-381. Pittsburgh, Pennsylvania: Materials Research Society.

Al and Bi are released at sub-stoichiometric levels that vary with pH and likely reflect surface precipitate formation of Al and Bi (hydr)oxides,

Bi-Si glass dissolution rates (Si-based) increase with decreasing pH and increasing temperature (E_a ~ 67 – 88 kJmol),

Bi-Si glass degrades at similar rates and by similar mechanisms to nuclear waste analogue glasses.

Low Temperature Synthesis and Sintering of U metal and U-La alloy Nanoparticles

- We have demonstrated the ability to fabricate nuclear fuels at low temperatures allowing for the formation of complex Uranium metal and alloys with minimum volatility of alloy compounds in the process

- This is of value because it potentially allows for the recycling of dissolved uranium and lanthanide ions from acidic solutions (used fuel) into metals and alloys

- Gamma (γ) irradiation is used to reduce uranium and lanthanide ions to metal Nanoparticles in solution at room temperature

- Successful metals made with U and UO_2; alloys made and characterized with U-Eu and U-La; these specific lanthanides were chosen due to their similarity in ionic size and charge (*J. Nuclear Materials* 442 (2013) 162–167)

- Our research has already shown that nanparticles sinter at much lower temperatures than Bulk metals due to their high surface area to volume (see data on UO_2 sintering at 500-600°C (700-1000°C lower than bulk; *Chem. Mater*. 2011, 23, 5185–5190.)

-low temperature sintering is vital for future mixed metal nuclear fuels as many actinides (eg., Am mp ~ 994°C) will volatilize during traditional high temp sintering process, and potentially result in release to the environment and/or other ES&H issues.

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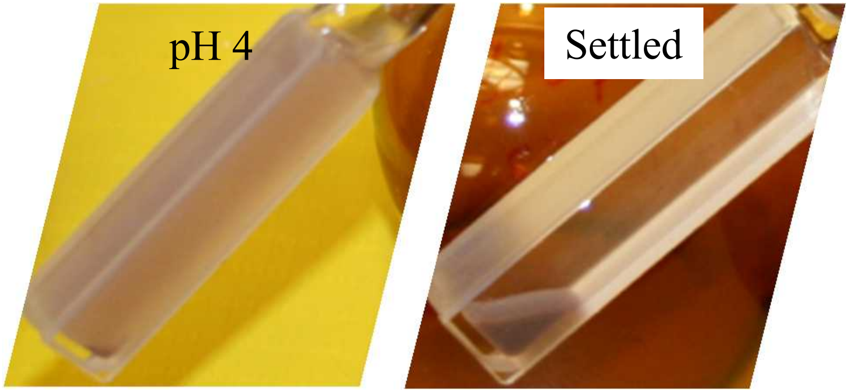
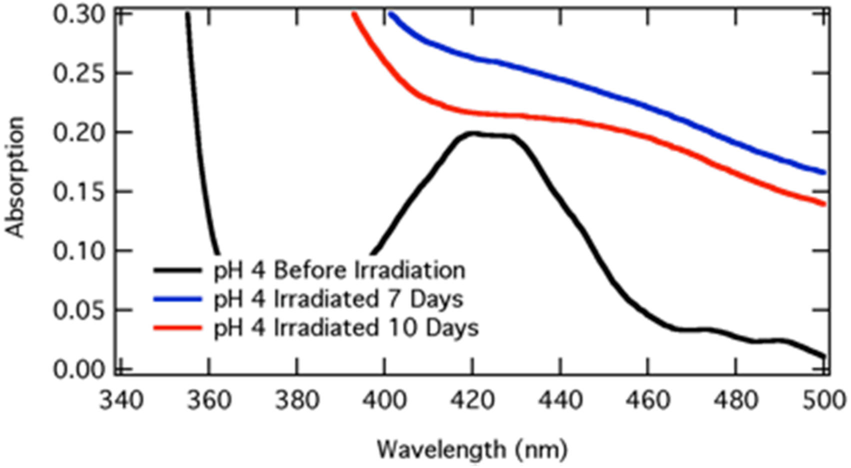
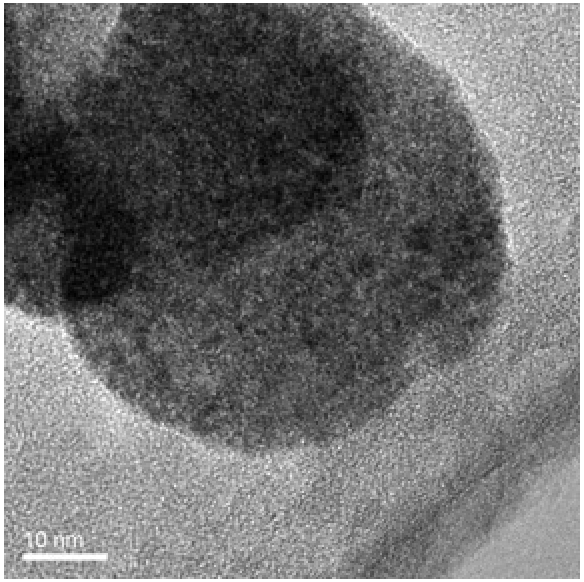
Lanthanide (metal, oxide) Nanoparticles

- **Radiolytic formation of actinide nanoparticles**
- Novel approach for nuclear fuels synthesis
- NPs are formed at RT, reduced sintering temps
- Reducing defect formations in bulk metals
- Normal sintering of bulk at 1500-1700°C



Experimental:
Uranyl nitrate in aq. solution, 10% alcohol (IPA), deaerated
Irradiated: 5 rad/sec 7-10 days





Chem. Mater., **2011**, 23, 5185
J. Chemical Physics, **2012**, *137*(7), 074502
J. Nuc. Materials, **2013**, *442*(1-3), 162

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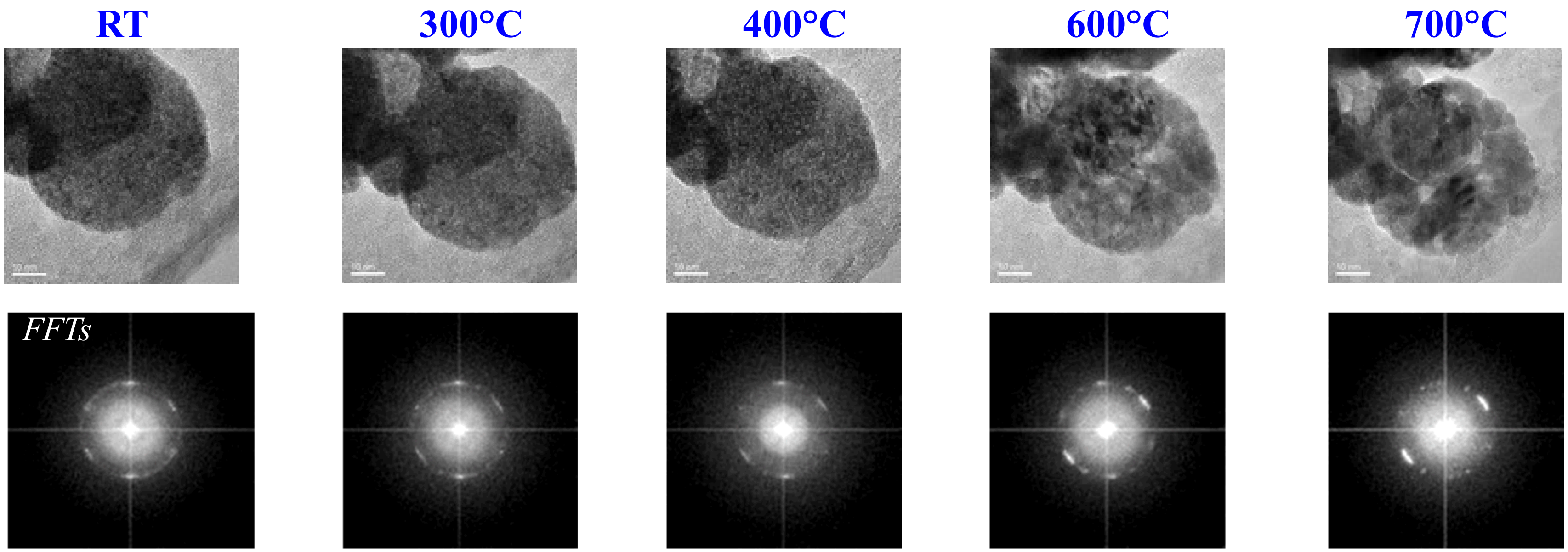
Lowered Temperature for Sintering of d-UO_2 NPs:

Dramatic decrease in sintering temp (< 600°C)

d-UO_2 NPs, Protochips Aduro™ holder, small scale ripening from RT-700°C



Diffraction Data, in Angstroms

RT	700° C	Lit. Values UO_2 41-1422	Lit. Values UO_2 36-89
6.51			
3.23	3.15	3.15	3.15
2.78	2.72	2.73	2.70
1.97	1.93	1.93	1.94
1.69	1.64		
	1.58		
	1.35		
	1.24		

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Ideas for collaboration between Saclay and Sandia

How can CEA-Saclay help us?
- High rad field studies
- Testing of adsorption and waste form materials with radiological ions and molecules

What does a collaboration look like?
- Exchange of ideas, students, staff, materials
- Joint publications
- External Advisory Board participation
- Joint international research proposals/programs

Open to new, additional exchanges

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Extra Slides

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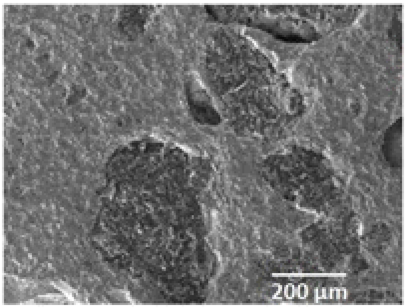
Low-sintering Temperature Glasses for ^{129}I Waste Encapsulation

- 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: Both AgI/glass and AgI-MOR/glass compositions were fabricated.

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

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



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

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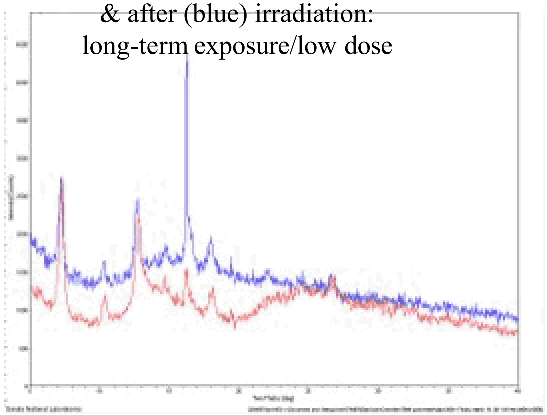
Irradiations stability testing of SNL Waste Forms at Sandia Gamma Irradiation Facility (GIF)

Sandia GIF

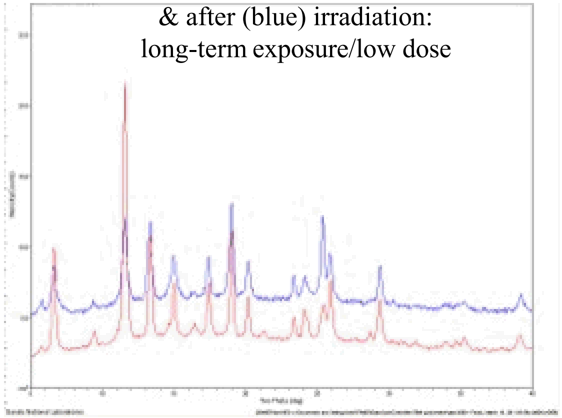
Dose rates:
-long-term exposure/low dose:
0.1 Rads/sec, with an overall dose of 2.59 x 10^5 Rads (2218Gy)
-short-term exposure/high dose:
800 Rads/sec, 1 x 10^6 Rads (10,000 Gy)

Samples tested include:
EG 2922 Glass (550°C), 87.5Glass/12.5SiO_2
80Glass/20AgI-MOR/10Ag
ZIF-8 (MOF), ZIF-8/I_2
HKUST-1(MOF), HKUST-1/I_2, Glass/HKUST-1/I_2
Bi-I-O

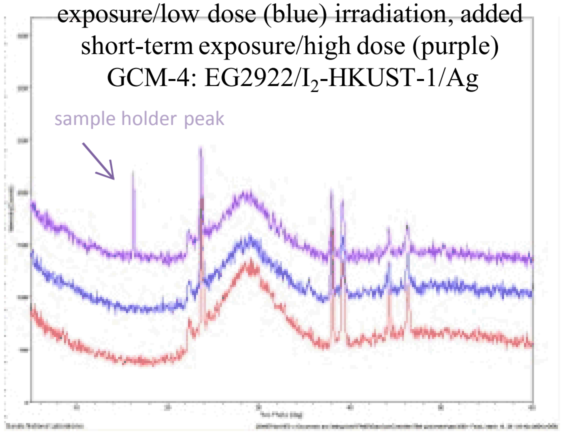
Examples of MOF irradiation studies:



90 wt.% I_2-loaded ZIF-8 before (red) & after (blue) irradiation: long-term exposure/low dose



I_2-loaded (≈100wt%) HKUST-1 before (red) & after (blue) irradiation: long-term exposure/low dose



GCM-4 before (red) & after long-term exposure/low dose (blue) irradiation, added short-term exposure/high dose (purple)
GCM-4: EG2922/I_2-HKUST-1/Ag

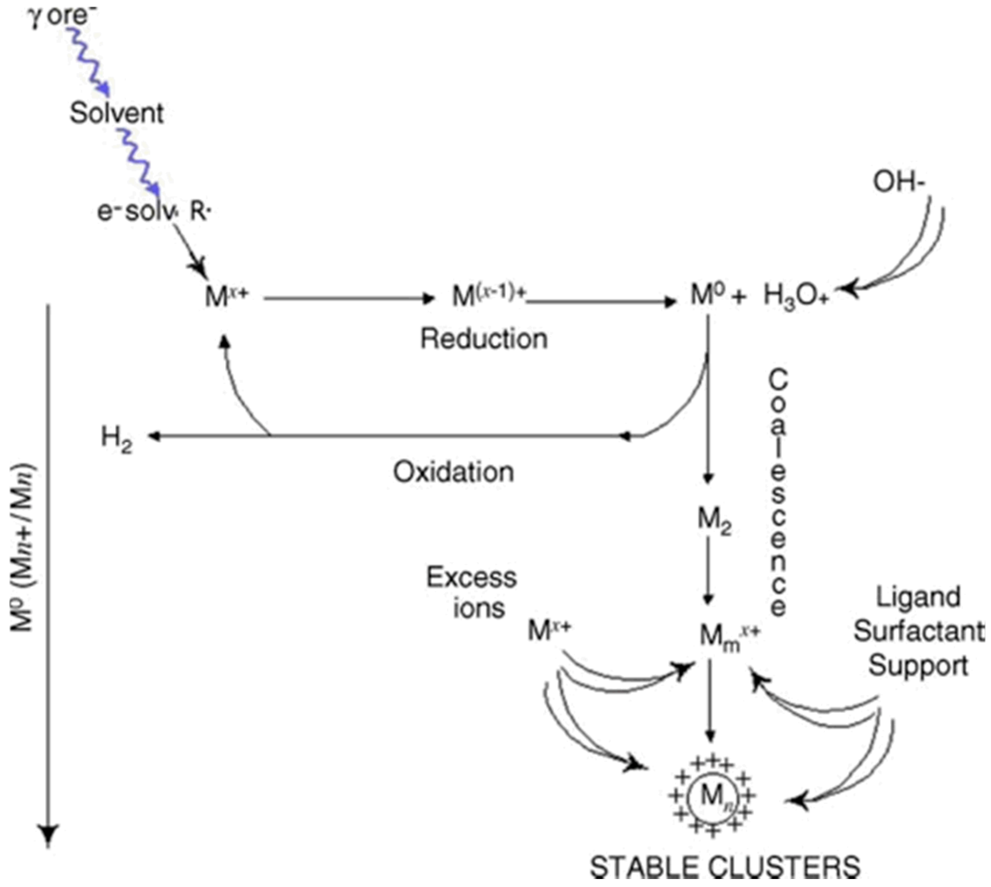
No structural changes as seen by XRD or in PCT responses of any samples. This radiological characterization is a good approximation of an adequately shielded long-term disposal environment.*

*R. H. Jones, Radiation Effects; A Compilation of Special Topic Reports, prepared for the Waste Package Materials Performance Peer Review submitted to U.S. DOE and Bechtel SAIC Company, 18-1 (2002).

Radiolysis Pathway for Nanoparticle Formation

Ion reduction by ionizing radiation:
Dose rate dictates [e^-] in reaction solution thereby affecting the chemistry of the NP formation

$H_2O \Rightarrow e^-_{aq}, H_2, OH^\bullet, H^\bullet, H_3O^+, H_2O_2, HO_2^\bullet$



Belloni, *Catalysis Today*, **2006**,*113*,141

Reaction Mechanism for d-UO_2 Nanoparticles

Particle formation via radiolysis (γ-irradiation)

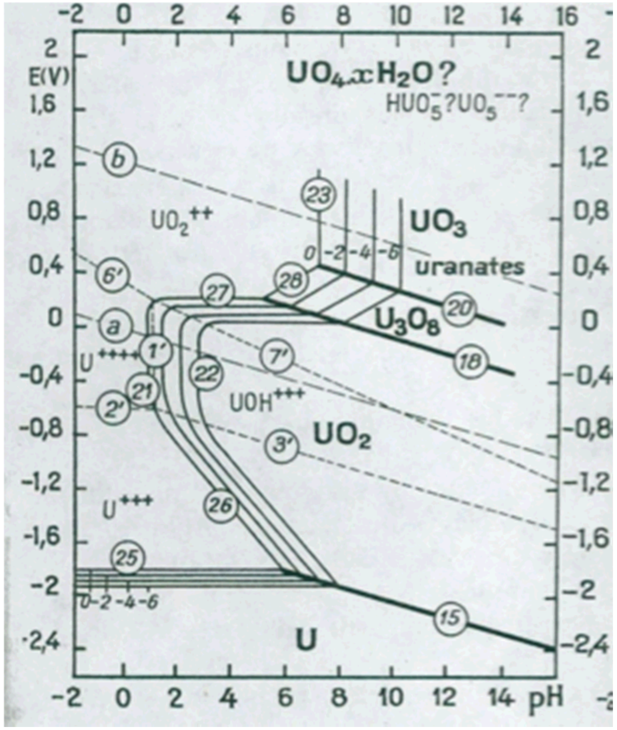
$^{\cdot}OH(^{\cdot}H) + e_{aq}^{-} + CH_3OH \rightarrow e_{aq}^{-}/\,^{\cdot}CH_2OH + H_2O(H_2)$

$e_{aq}^{-}/\,^{\cdot}CH_2OH + UO_2^{2+} \rightarrow UO_2^{0} + \,^{\cdot}CH_2OH$

Particle growth

$x\,^{\cdot}CH_2OH + (UO_2)_n \rightarrow (UO_2)_n^{x-} + xCH_2O + xH^+$

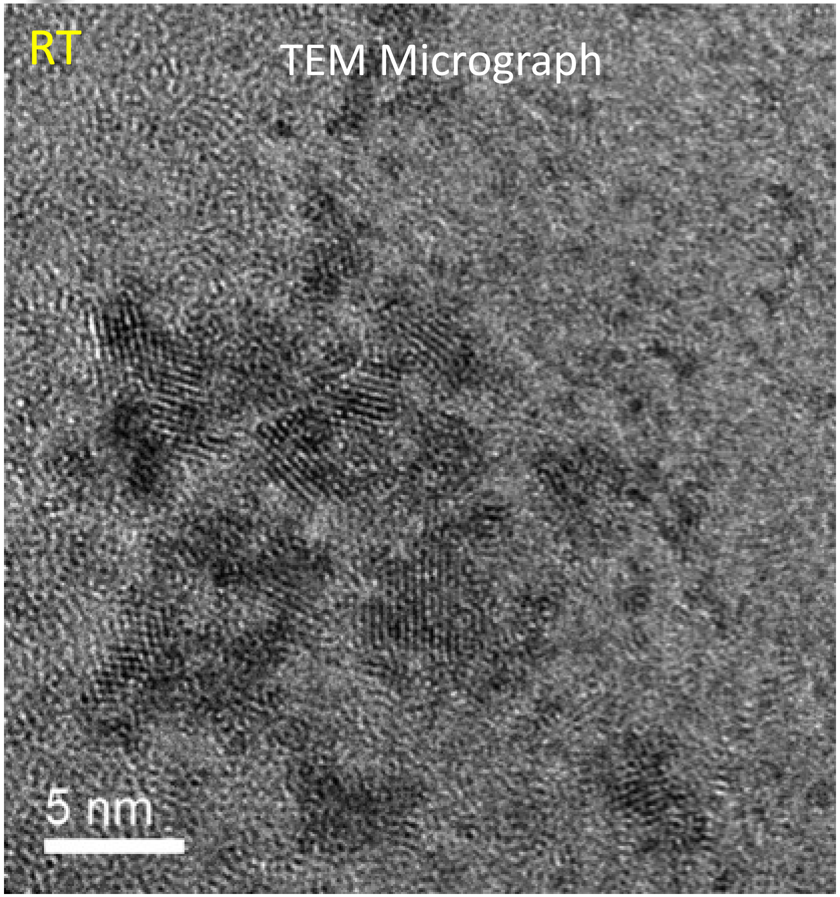
Pourbaix Diagram



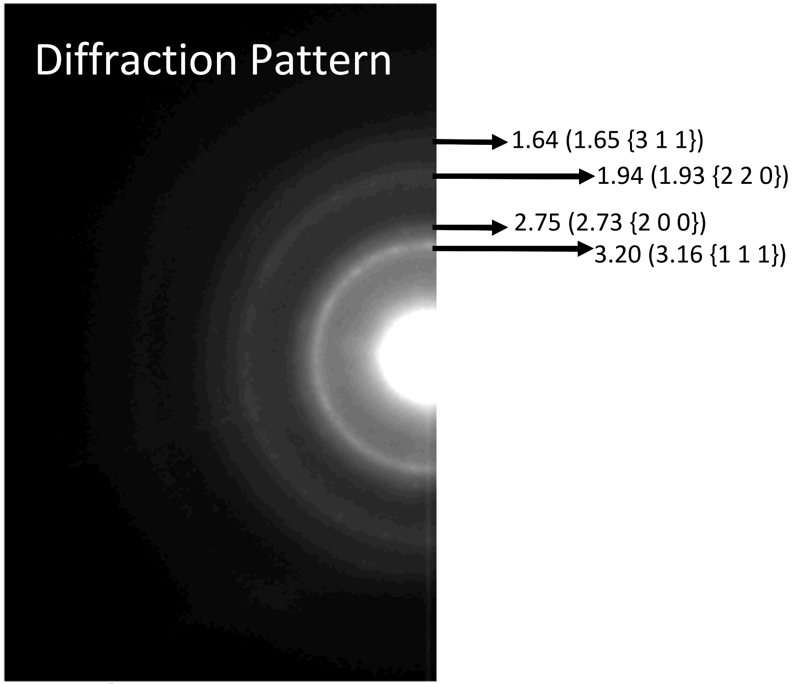
Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions; 1974.*

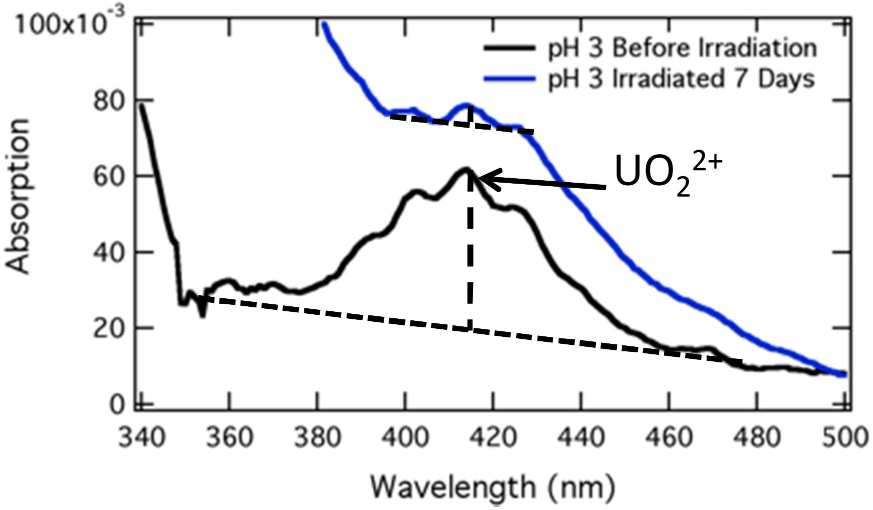
Aqueous room temperature synthesis to form NPs

Characterization of UO_2 NPs Formed at pH 3



UO$_2$ NP formation confirmed by UV-vis, bright-field TEM and diffraction





Low-Temperature Sintering Glass Composite (GCM) Waste Forms

- Glass Composite Materials (GCM): versatile "any I_2 getter" *universal waste forms* with high flexibility of the materials incorporated: metals, zeolites, MOFs etc.

- Glass compositions of Ag containing iodine-getter materials *need to have melting points below 558˚C* (AgI melting point)

- Targeted waste form:

✓ compact and monolithic

✓ mechanically, thermally, and chemically stable

✓ able to sustain compatibility with various repository conditions

- Current Effort: determine degradation rates of the GCM (Glass + AgI) through Single Pass Flow Through Testing at variable temperatures and pH; and durability with PCT and MCC-1 testing

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PCT results

Bi-Si-Zn 550°C sintering glass
High durability/stability

PCT Test**: 90°C, 7 days, DI water

Composition	B	Na	Si	K	Zn	Ag	I	Bi
BiSi-Glass	0.6	3.4	1.9	1.4	0.6	0.0	0.02	0.08
BiSi-Glass (75wt%)/AgI (25 wt%)	0.7	1.5	1.9	0.8	1.2	0.0	2.3	0.02
BiSi-Glass (80wt%)/AgI-MOR(20wt%)/Ag(+5wt%)	8.6	6.5	5.6	0.4	0.05	7.7	0.3	2.2

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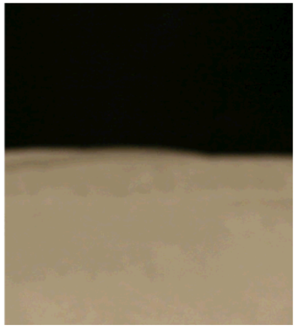
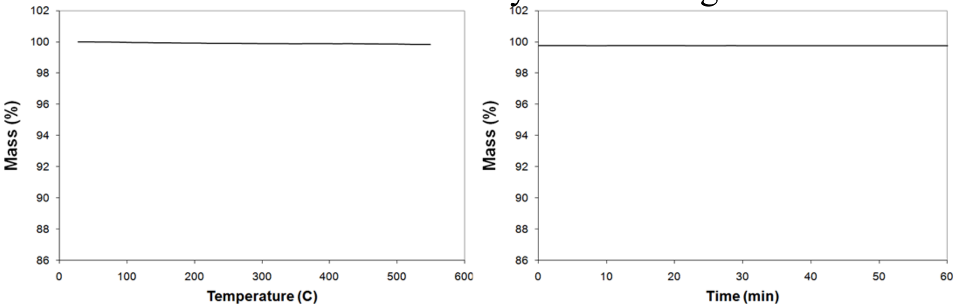
Verify fabrication of Glass Composite Material (GCM) Waste form: Glass/AgI



50 wt% Glass
50 wt% AgI

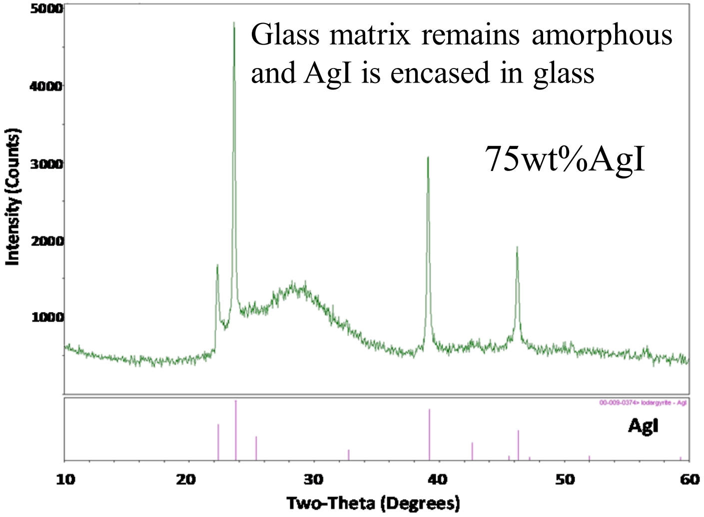
GCM Waste Form: AgI and mixed with glass.
Sample uniaxial dry pressed at 70 MPa in steel die.
Sample heated 10°C/min in air, 550°C, 1 hr

Thermal Stability of Glass/AgI



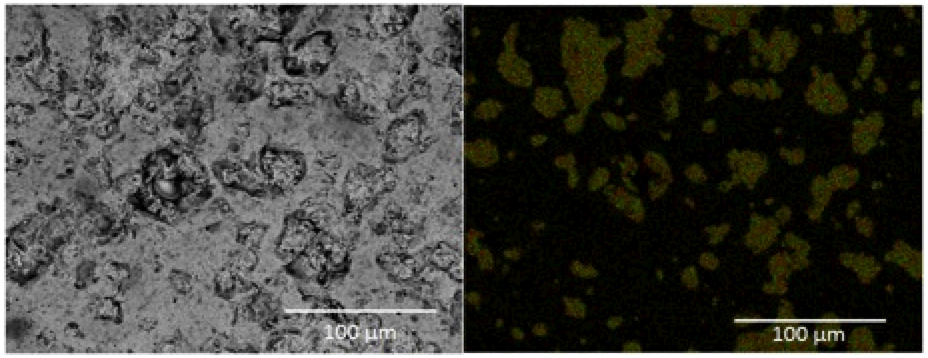
TGA: heating 10°/min

Held at 550°C, 1hr



Glass matrix remains amorphous and AgI is encased in glass

75wt%AgI



SEM/EDS map
I confined to AgI spots

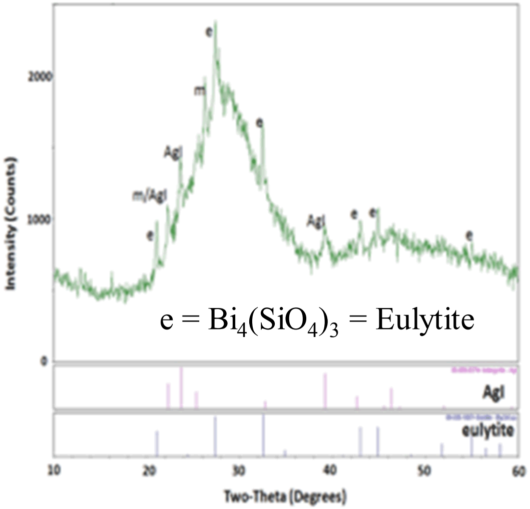
Glass Composite Material (GCM): Glass/AgI-MOR, Homogeous WF

AgI-GCM preparation* for reference technology studies:

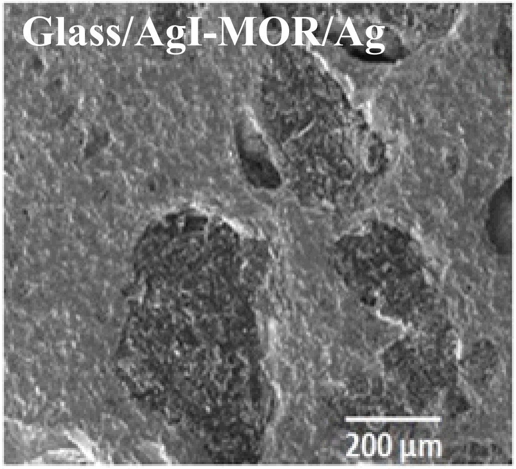
AgI-MOR ground in mortar and pestle, then sieved to <150 µm.
Mixed at 20wt% with 80 wt% glass powder and additional 5wt% Ag flake.
Uniaxially dry pressed at 70 Mpa in steel die.
Heated at 2°C/min in air to 550°C for 1hr to sinter.

Final composition: 76.2%glass, 19% Iodine loaded Ag-MOR, 4.8% Ag

*J. Amer. Ceram. Soc. **2011**, *94*(8), 2412-2419.



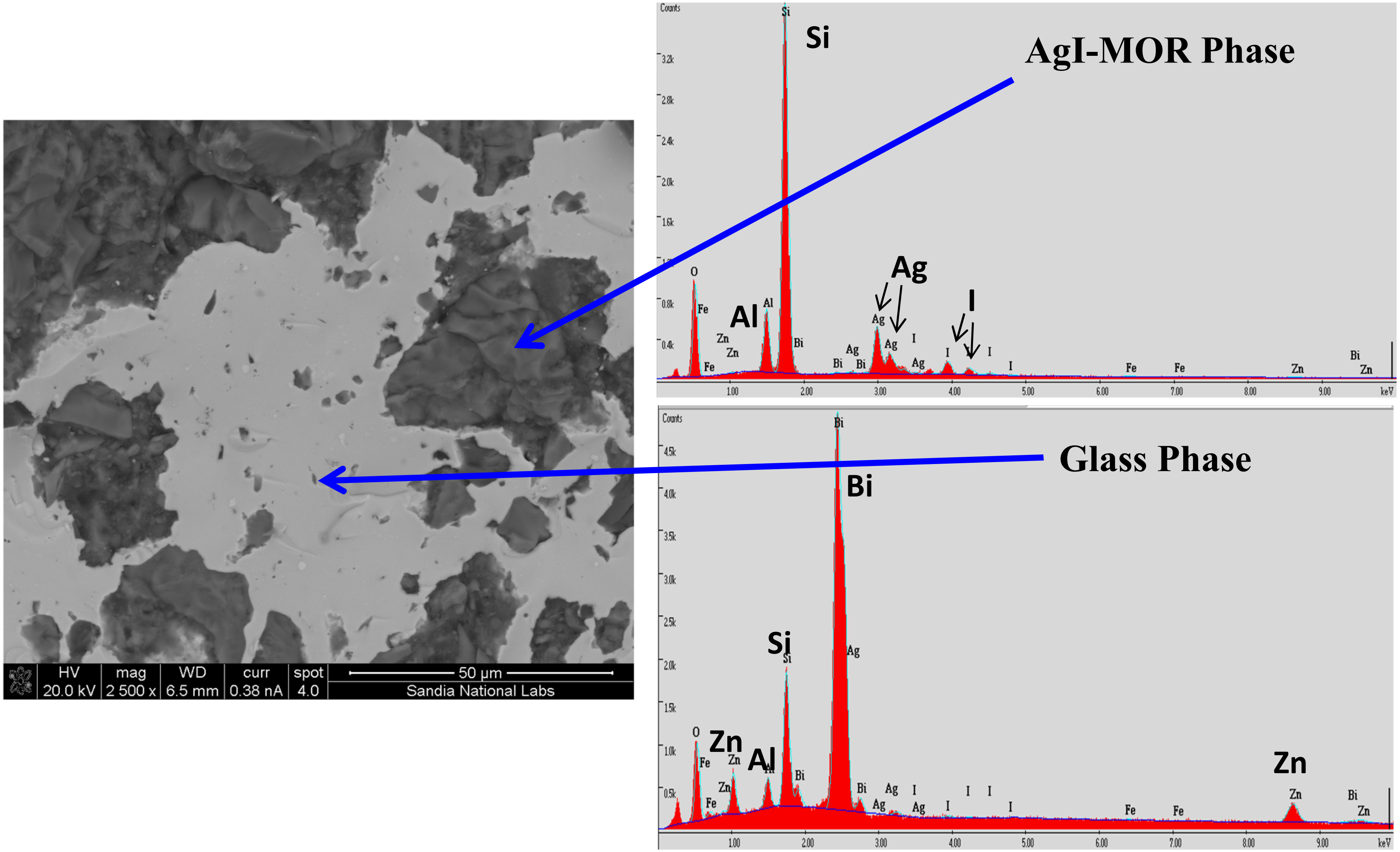
e = $Bi_4(SiO_4)_3$ = Eulytite



Complete Physical Encapsulation of AgI by Glass in composite

T. M. Nenoff, tmnenof@sandia.gov

GCM Microstructure:
AgI-MOR isolated by dense glass matrix



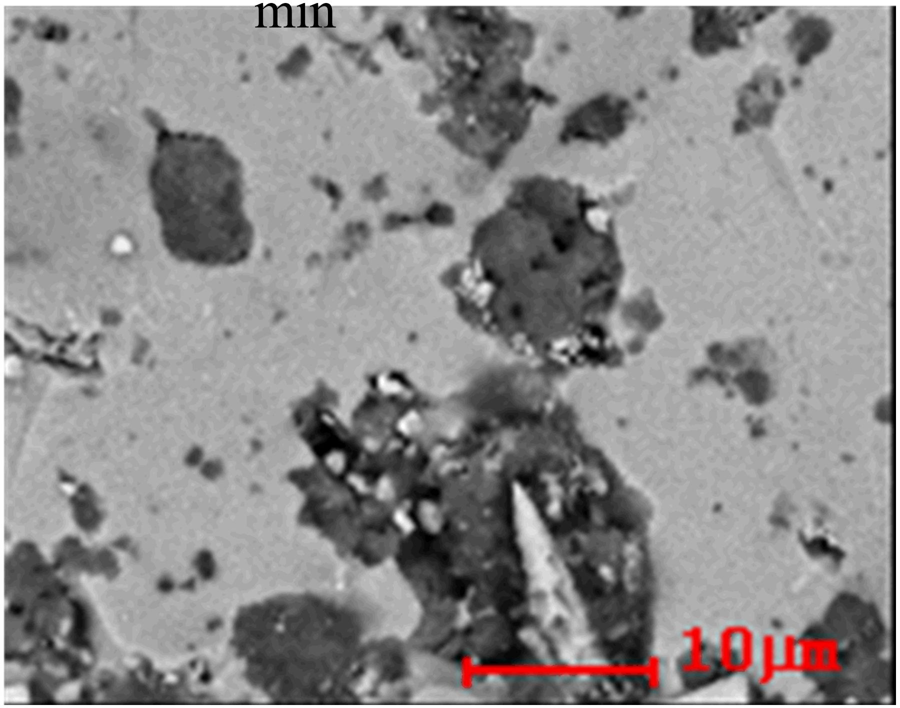
AgI-MOR Phase

Glass Phase

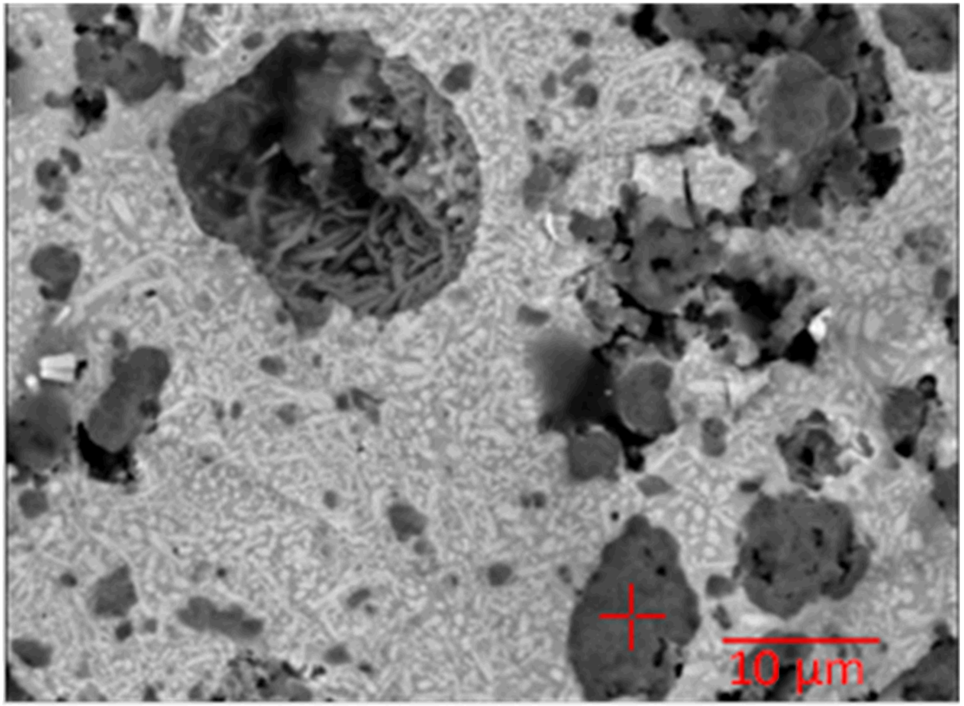
Sintering temperature: Avoid (1) Iodine release with AgI melt, (2) phase mismatch

15 wt% AgI-MOR samples

550°C for 20 min



575°C for 1 hr



575°C: Eulytite Crystals are acicular & uniformly distributed in the GCM glass phase

Durability Testing: PCT and MCC-1

PCT, ASTM C1285 : samples of each composition were ground with mortar and pestle and sieved to between 75 and 150 m for Product Consistency Testing (PCT). 1 g of ground material along with 10 ml of deionized water were placed in a PTFE container that was then sealed and heated at 90°C for 1 week.

MCC-1, ASTM C1220: monolithic leach testing. A pellet of nominally 1 cm in diameter and 2 mm thick with flat surfaces ground to 600 grit along with 20 ml of deionized water were placed in a PTFE container that was then sealed and heated at 90°C for 1 week.

Duplicate samples were run for each composition for both types of test. A blank that contained only deionized water was also run at the same time.

SPFT, PCT and MCC-1 effluents were analyzed for pH, and for Ag, I, Zn, and Si by ICP-MS in semi-quantitative mode and represent the average of 12 readings

PCT and MCC-1 leach tests: Performed on both Amorphous & Crystallized Samples

PCT (Product Consistency Test): Granules in DI water for 7 days at 90°C.

Leachate Analysis Results (ppm)

	Si	Bi	Zn	Al	I
Amorphous	**20.3**	**0.021**	**14.6**	**0.234**	**0.002**
Crystallized	**18.4**	**0.064**	**98.7**	**0.494**	**0.001**

MCC-1 (Static Leach Test): Monoliths in DI water for 7 days at 90°C.

Leachate Analysis Results (ppm)

	Si	Bi	Zn	Al	I
Amorphous	**38.3**	**0.10**	**75.2**	**6.0**	**0.0007**
Crystallized	**20.1**	**0.017**	**84.0**	**1.2**	**0.007**

- Very low iodine levels in all leachates.
- Higher Zn concentration in leachate from crystallized sample.

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Post MCC-1 testing: Samples had Bi_2O_3 crystals of their surfaces.

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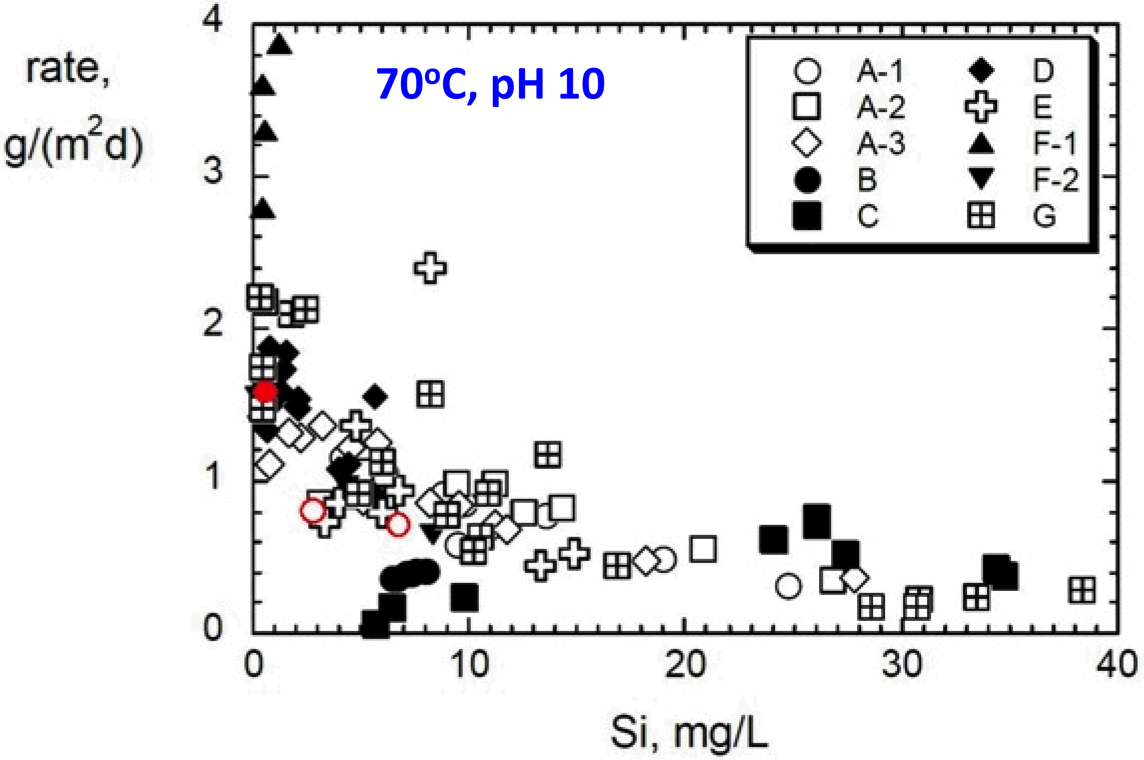
Benchmark SPFT Method Against LRM Glass Results

Steady-state LRM Glass Degradation Rates



LRM glass surface area = 0.021 m^2/g (0.2 g); Input solution - 0.004 molal LiCl/0.003 molal LiOH; q/S = 3.1 x 10^{-7}, 9.0 x 10^{-7}, and 1.0 x 10^{-5} m/s; effluent Si - 0.3 to 7 ppm.

Black/White Symbols– Inter-laboratory comparison of LRM glass dissolution rates of Ebert (2005) *Interlaboratory Study of the Reproducibility of the Single-Pass Flow-Through Test Method: Measuring the Dissolution Rate of LRM Glass at 70°C And pH 10*, Argonne National Laboratory. **ANL0-5/33**.

Red Symbols – Sandia-measured LRM glass dissolution rates.

Sandia Single Pass Flow Through Tests Produce Accurate Glass Dissolution Rates

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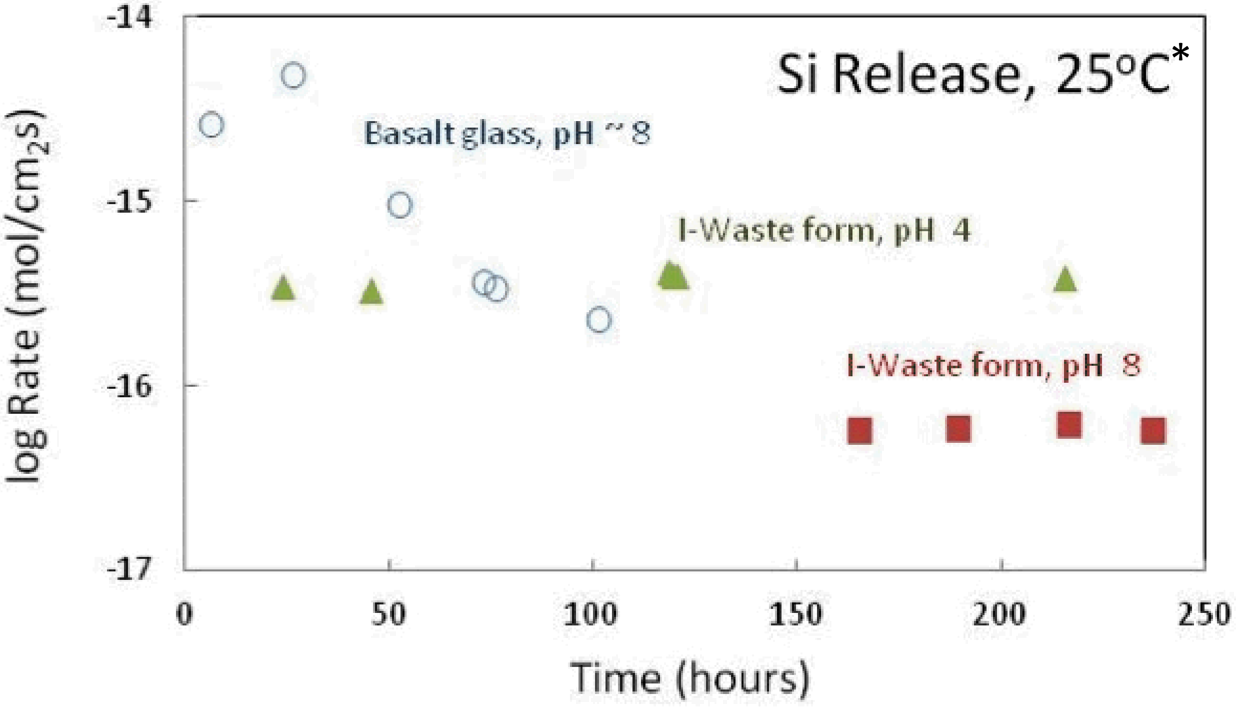
Si Release from Basalt Glass and I-Waste Form (Si release per total surface area)



*For normalization of GCM degradation rates to GCM surface area, divide by 0.79

Basalt glass is a natural analogue for waste glasses
I-Waste form Si release similar to that of basalt glass at pH 8
Si release increases at lower pH
Zn release increases at lower pH (not shown)

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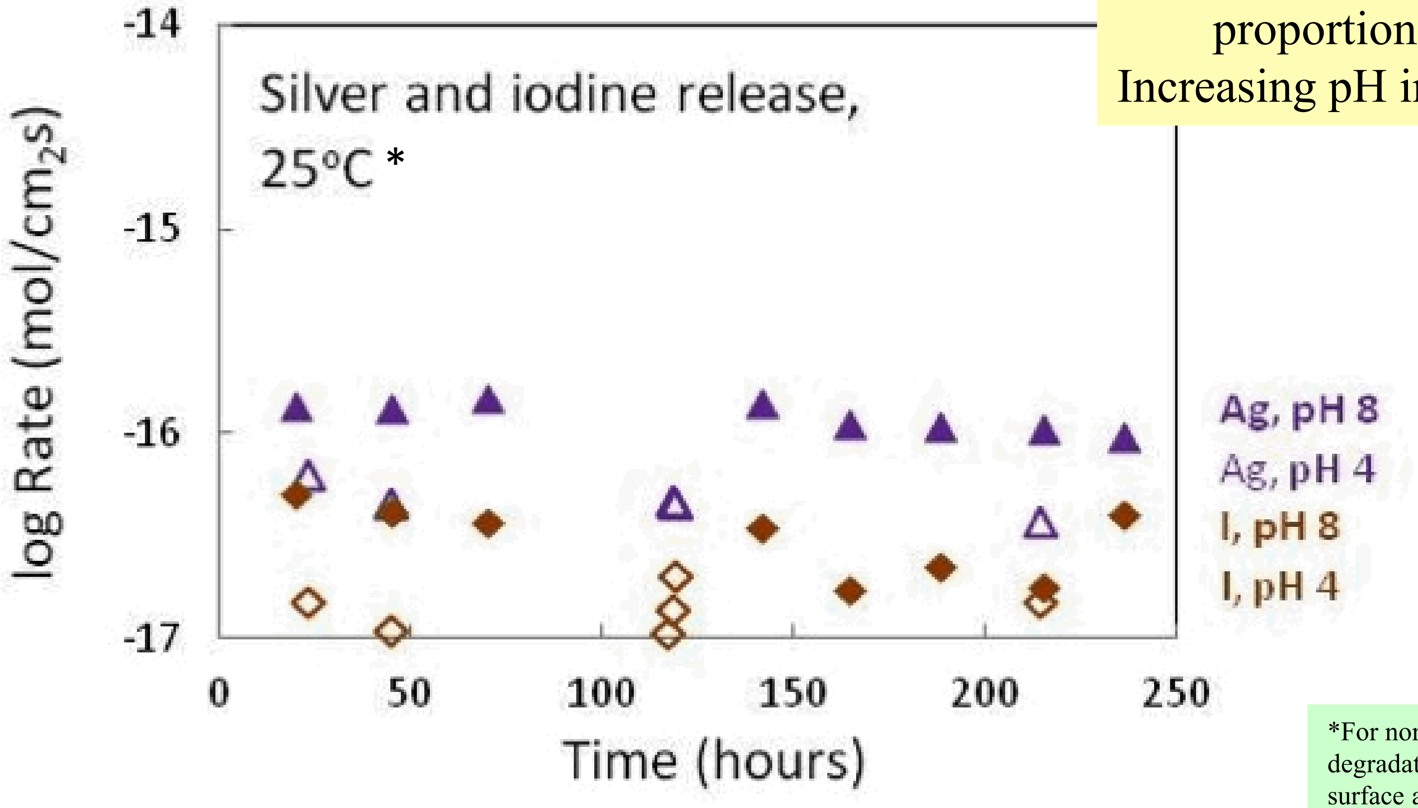
Silver and Iodine Release from I-Waste Form

Silver and iodine release is low
(< 10^{-15} mol/cm^{2}s)

Silver and iodine release is
proportional

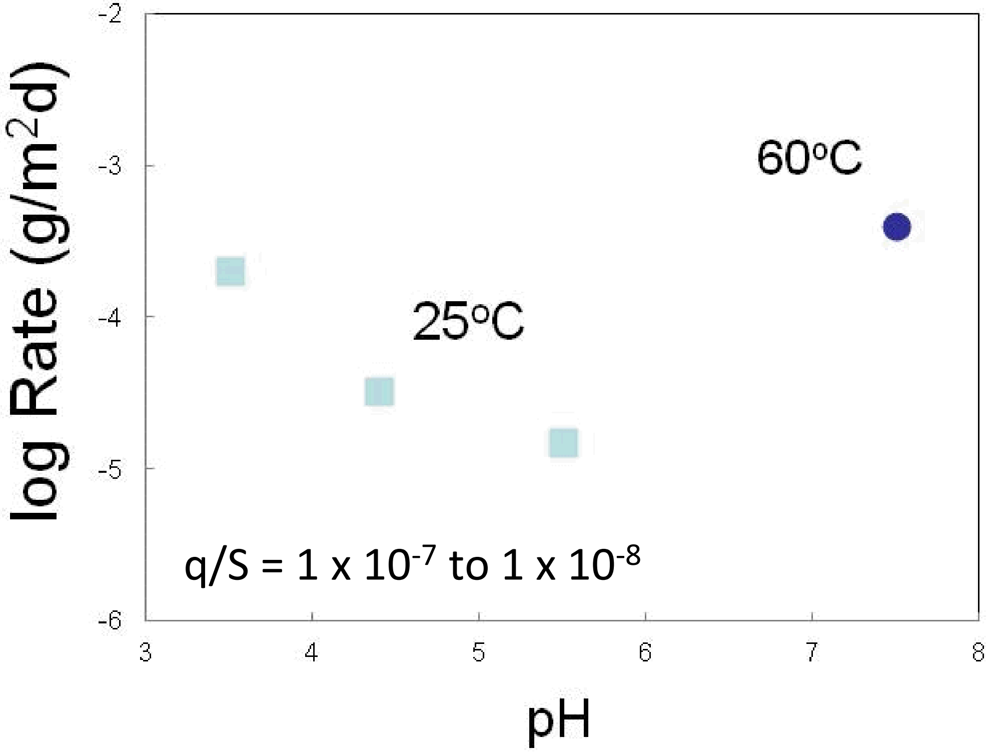
Increasing pH increases release



*For normalization of AgI degradation rates to AgI surface area, divide by 0.25

Effect of pH AgI-Mordenite Dissolution

Steady-state AgI-Mordenite Degradation Rates*



*calculated from silica release.

AgI-Mordenite dissolution (Si-based) increases with decreasing pH and with increasing temperature (E_a ~ 70) kJ/mol) but is slower than glass degradation,

Ag and I release from AgI-Mordenite <u>decreases</u> with decreasing pH.

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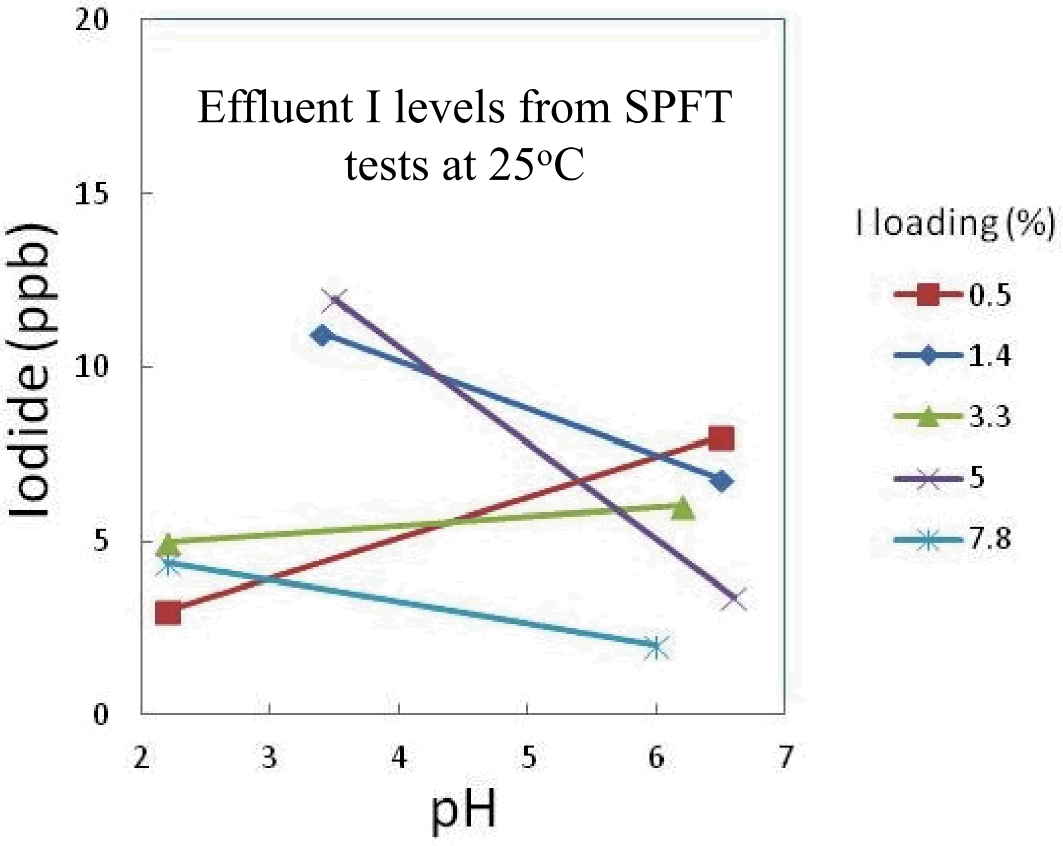
Iodine Loading and Iodine Release from GCM



There is no clear effect of Iodine loading on Iodine release.

Iodine levels vary less than a factor of 4 from pH 2 - 7; and I loading 0.5 - 7.8%

***Low Level* I release is likely controlled by AgI solubility.**

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

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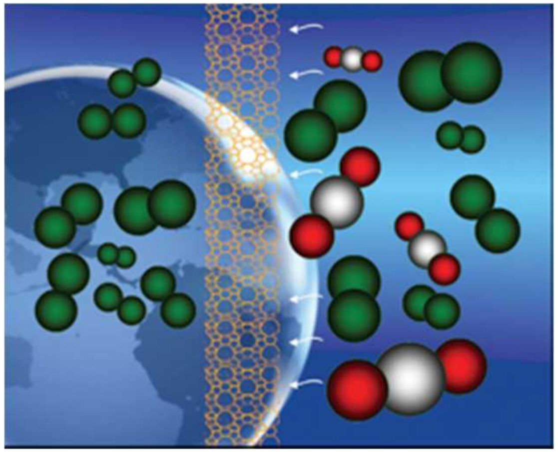
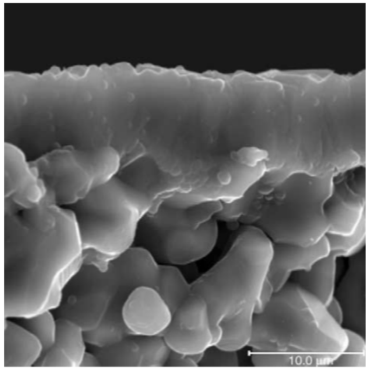
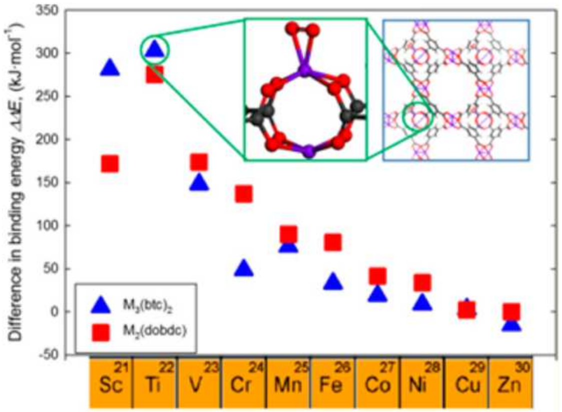
Example 2: Zeolite/MOF Membranes for Light Gas & Hydrocarbon Separations

H_2 Purification
Nature Mater., **2015**, *7*, 377; *Chem. Rev.* **2007**, *107*, 4078
MRS Bulletin, **2006**, 31(10), 735 (cover; Editor Nenoff)



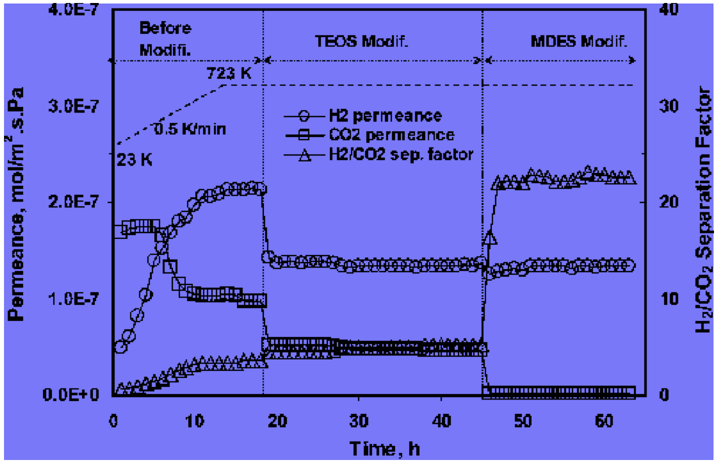
ZSM-5 Zeolite membrane for
H_2 from CO_2 separations
Micro Meso Mater, **2003**, *66*, 181





O_2 Separations with MOFs for Energy Efficient Oxyfuel Combustion

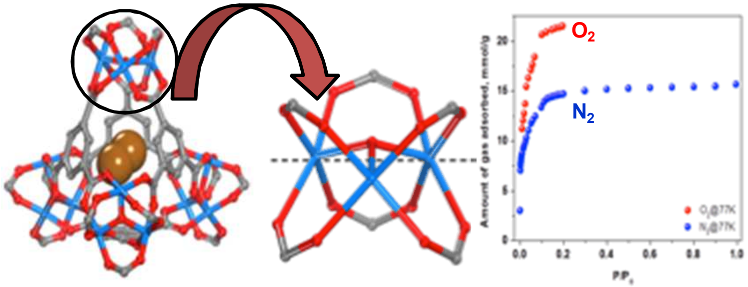
Chem. Mater. **2016**, in press
Chemical Science **2016**, *18*, 11528
J. Phys. Chem. C, **2015**, *119,* 6556
Chem. Mater. **2015**, *27*(6), 2018



H_2 Purification from Syngas
Langmuir, **2009**, *25*(9), 4848

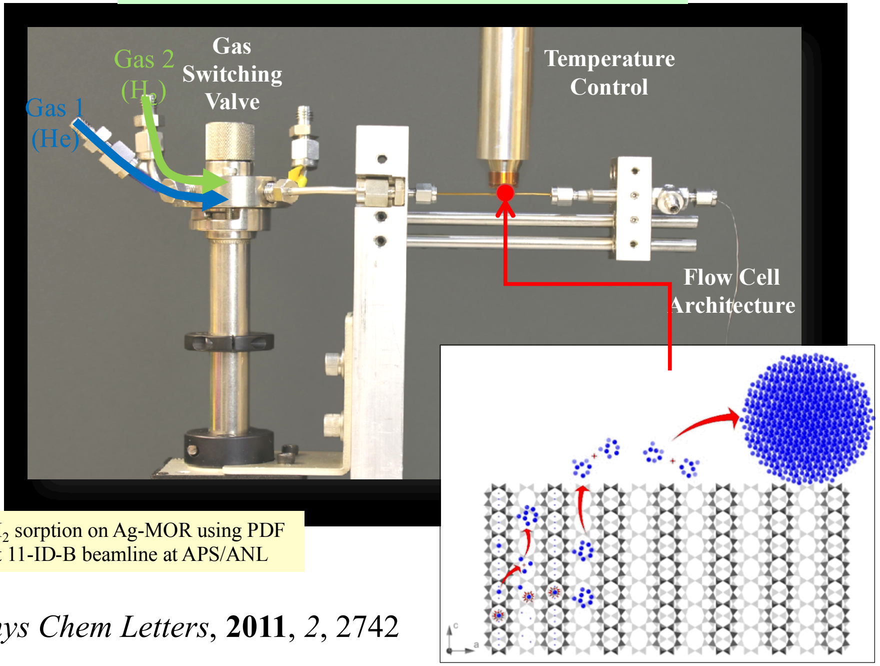
O_2@Sc-MIL-100

O_2>N_2 @77 K – 313 K



Example 3: Nanoporous Zeolites for Heterogenous Catalysis and Subsequent Gas Capture

Determine Mechanism of Ag^+ to Ag° NPs in MOR

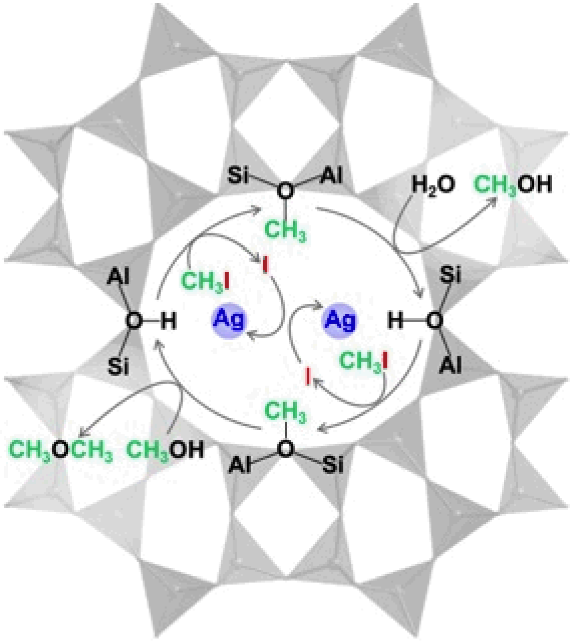


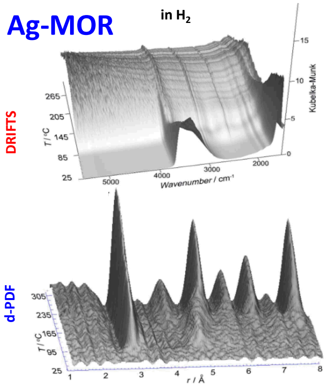
In situ I_2 sorption on Ag-MOR using PDF setup at 11-ID-B beamline at APS/ANL

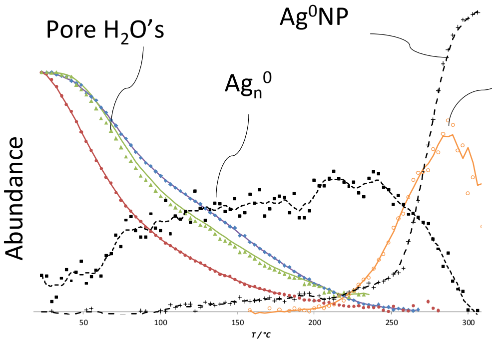
J Phys Chem Letters, **2011**, *2*, 2742

Mechanism of Iodine Capture on Ag-MOR from Acidic Humid CH_3-I Stream: Catalytic Cleaving of CH_3-I and I Capture

Micro. Meso. Mater., **2014**, *200*, 297 (invited)







Initial Data, Ag-MOR in H_2: Correlation identified between –OH surface functionalization and Ag migration to the outer surface of the MOR

On-going: Combining complementary insights from simultaneous IR and PDF.
For mechanism of NP catalyst formation

Chapman & Nenoff **2016**, in preparation