U.S. DEPARTMENT OF ENERGY | Nuclear Energy

SAND2011-2798C

The Fuel Cycle Research & Development

Iodine Confinement into Metal-Organic Frameworks (MOFs)- Novel Nuclear Waste Forms

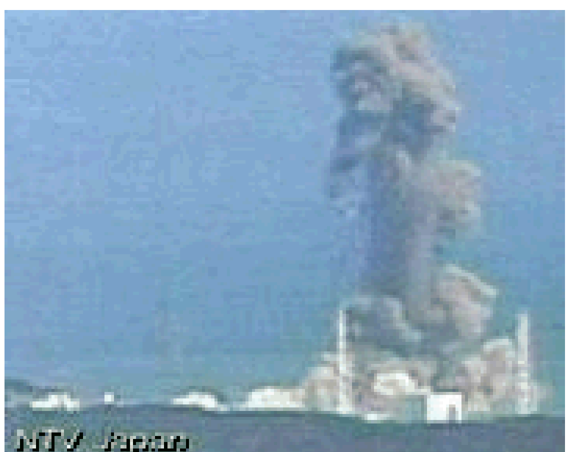
Tina M. Nenoff, Dorina F. Sava, Terry J. Garino

Materials Research Society:
Crystalline Nanoporous Framework Materials-
Applications and Technological Feasibility
Emerging Applications,
Tuesday, April 26th, 2011

This project is funded under the DOE/NE-FCR&D Separations and Waste Form Campaign.

Volatile Gases: Separations and Storage Needs in Nuclear

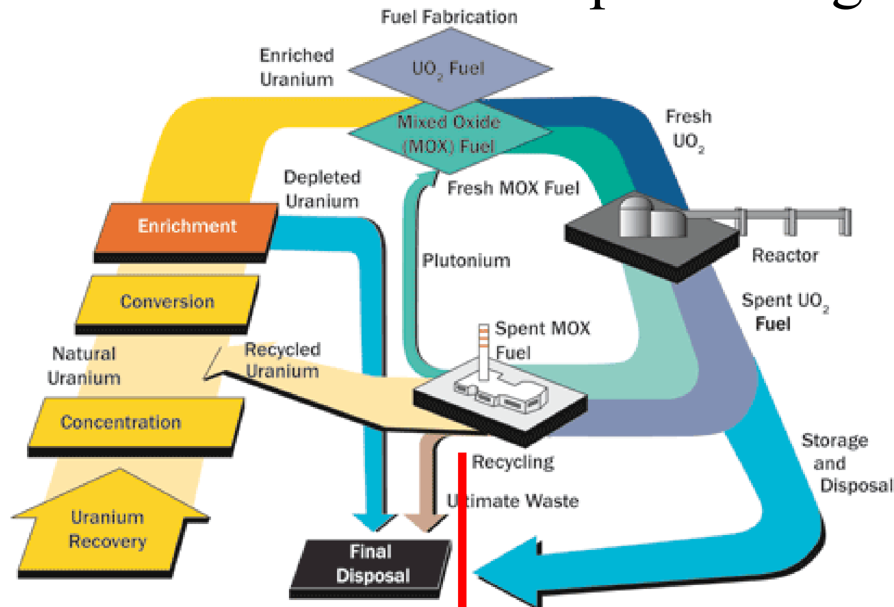
I. Nuclear Waste Legacy



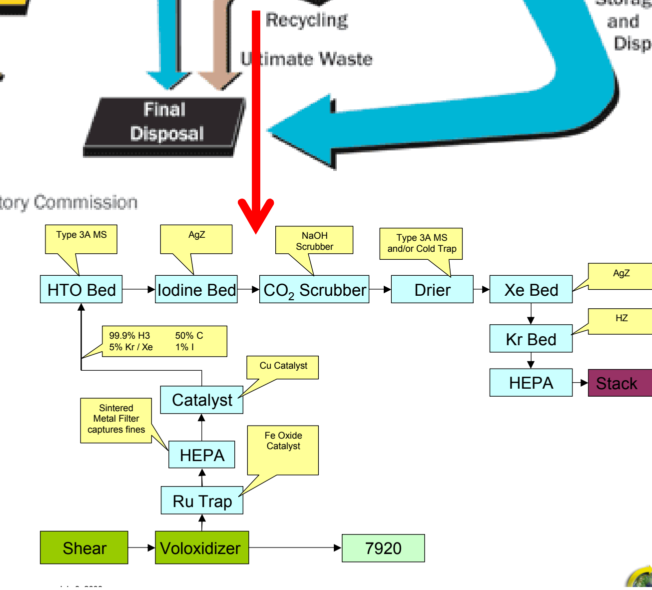
Fukashima Daiichi Nuclear Power Plant explosion March 11, 2011
I^{129}, I^{131} volatile gas released

(www.IAEA.org)

II. Nuclear Fuel Reprocessing



Source: U.S. Nuclear Regulatory Commission

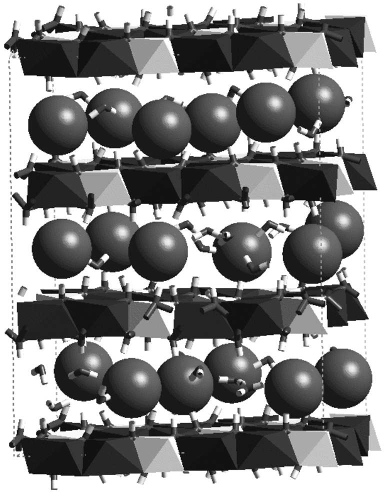


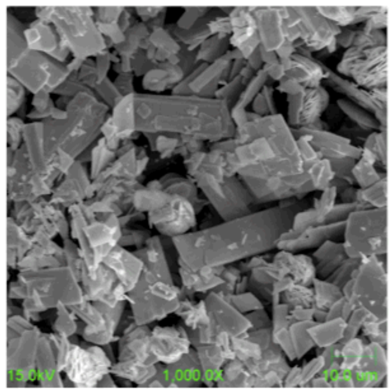
Volox, Dissolution
(post fuel crush, dissolving Hot HNO_3)
R. Jubin, ORNL

T.M.Nenoff, tmnenof@sandia.gov

Examples of SNL Waste Forms for Iodine Storage

Iodine from solution: Bi-I-O Hydrotalcites

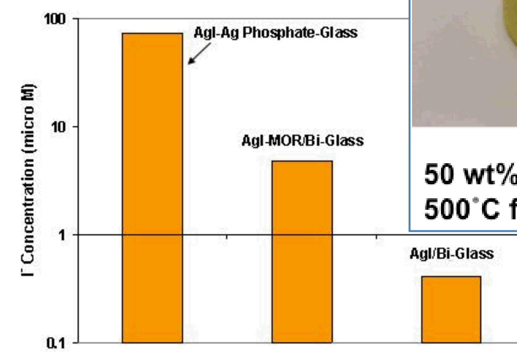




Applied Geochem, 2011, 26, 57.;
US Patent filed 2010

AgI off-gas, Ag-I-MOR Low temperature glasses

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



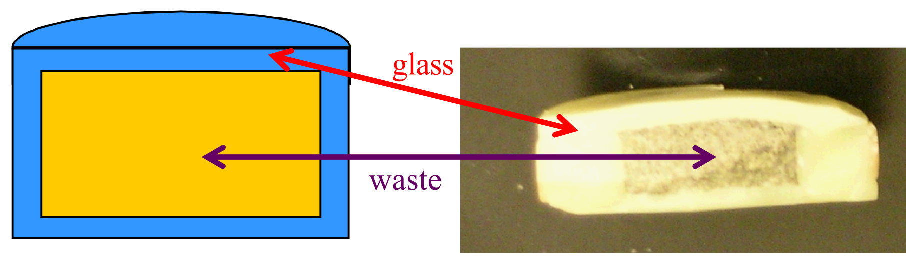
Leach tests
90°C, 7d, DI H_2O

Ceram. Trans. **224,** 305*; US Patent file 2010*

Ag-I-Hybrid Materials + Low temp glasses

Ind. Eng. Chem. Res, 2011, in press

Core-Shell Glass Waste Forms



Shell: 100% Glass; Core: Glass : AgI-MOR (250 to 600 µm) : Ag
J. Amer. Ceram. Soc. **2011**, in press

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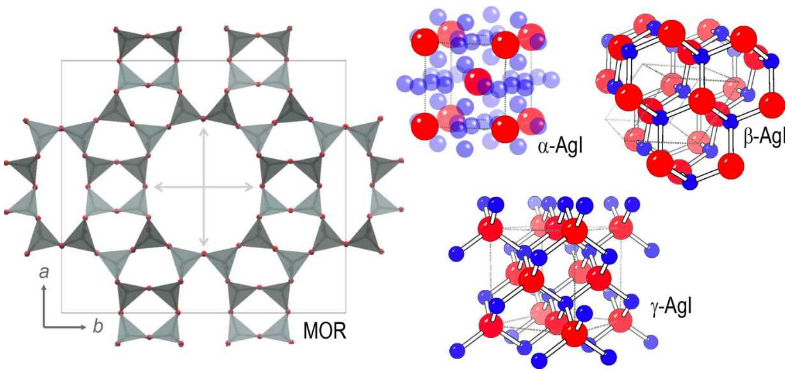
Volatile Radio-Iodine: Capture and Long-Term Storage

- Volatile gases/long-lived fission products pose *unique scientific issues* with regards to long-term storage
- ^{129}I is present in small concentration, however it has a half-life of 1.57 x 10^{7} years; 131I is short half life (8 days) but involved with human metabolic processes. *capture is very important*
- The leading technology: Ag-loaded zeolites, which capture the iodine mostly as AgI
- AgI is very insoluble, but it *is not geologically stable* at either the earth's surface or under normal repository conditions
- Additional separations processes/materials and novel *waste forms need to be developed for* permanent disposure in geologic repositories

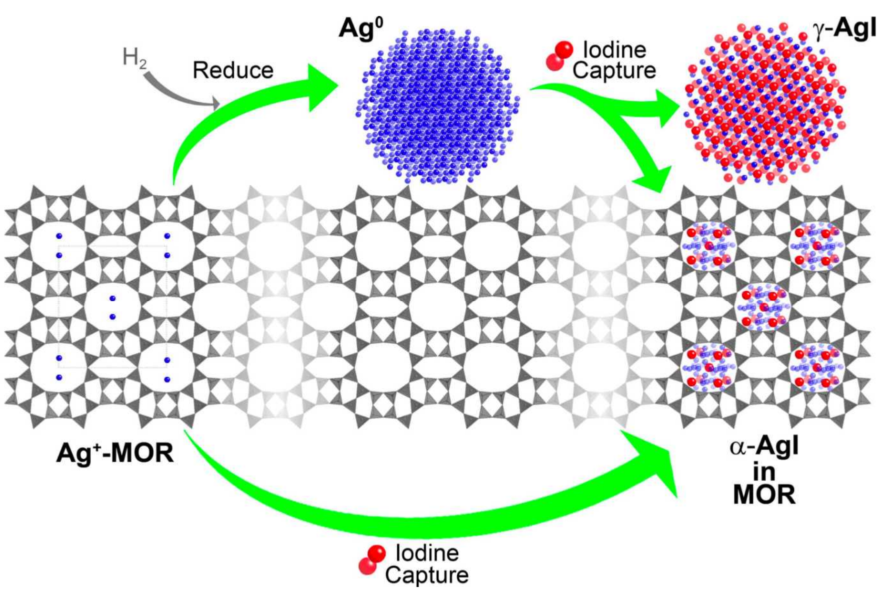
Crystalline frameworks for Iodine Sorption: Zeolites vs. MOFs



Historically, Ag-Mordenite Zeolite is Iodine soption material of choice.
Idealized MOR framework: $Na_2Al_2Si_{10}O_{24}$•$7(H_2O)$

1D channels (12-rings, 6.5 x 7.0 Å) which contain exchangeable cations and water molecules
α, β, γ-AgI polymorphs (iodine-red; silver-blue)

Max: 20 wt% I_2 loading in MOR zeolite



Structure-Property Studies w/ PDF:

Ag°-MOR + I_2 yields a mixture of γ-AgI bulk surface nanoparticles and sub-nanometer α-AgI.

Ag^+-MOR + I_2 produces exclusively sub-nanometer α-AgI ("**perfect fit**", confined in pores)

JACS, **2010**, *132*(26), 8897

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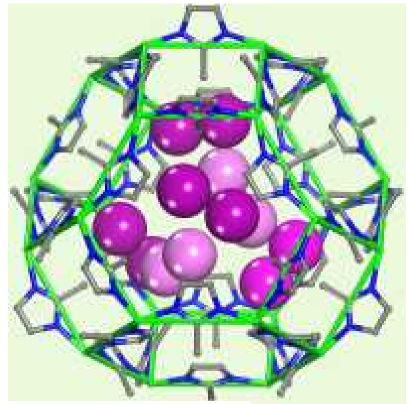
MOFs for Volatile Gas Capture, and Possible Short-Term Storage

$Zn(MeIM)_2 \cdot (DMF) \cdot (H_2O)_3$, ZIF-8

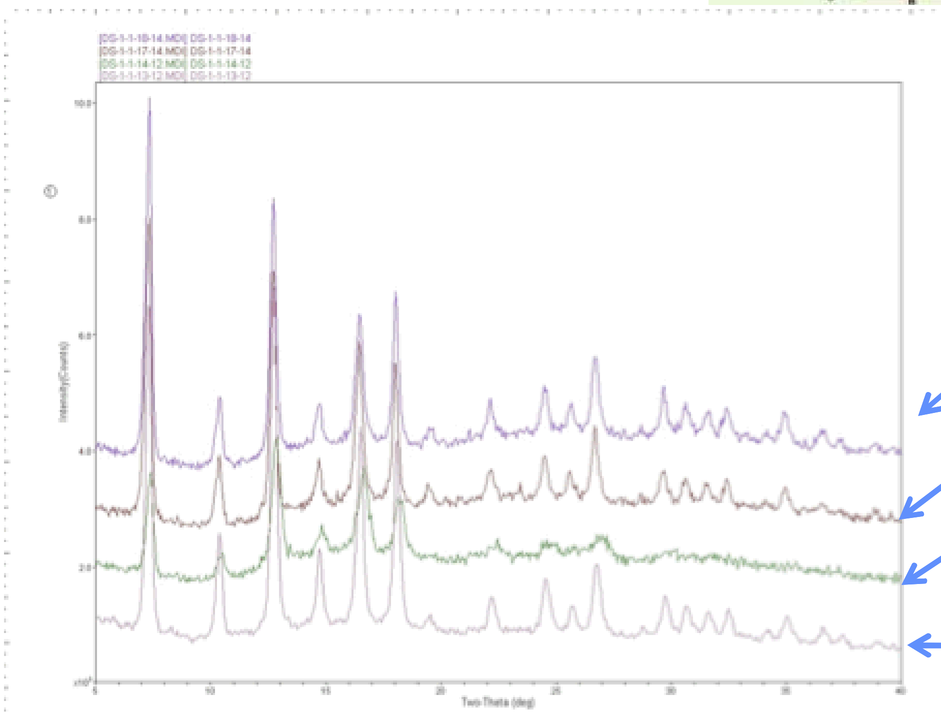
I_2@ ZIF-8 Structure Determination

Sava, et. al., submitted, 2011;
2011 MRS: UU 12.2, Thurs, 1:45pm.



SODALITE – like cages
Single Crystal X-ray structure of ZIF-8
Surface area: BET 1630 $m^2\ g^{-1}$
Thermal Stability ≤ 550°C

1.1 nm pore cavity
Pore opening ≈ 3.4 Å
I_2 effective radius ≈ 3.32 Å
Possible size selectivity with Org-I cmpds



I_2 vapor loading, 95°C, 84.7%, 91.7% wt loading

0.1M I_2/Benzene, washed, Dried, 65°C, 2hrs; 46wt % loading

0.1M I_2/cyclohexane, washed, Dried, 65°C, 2hrs 90wt % loading

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Waste Forms by Design: Low -Temperature Sintering Glasses

- For Iodine Storage: utilized chemistry of glasses and sorption materials to durably store the iodine during decay.

- Known iodine getters include Ag, Ag-Zeolite. Temperature dependence of AgI (mp =558˚C) dictates temperature processing limit of waste form

- Volatile Gas Sorption by MOFs: waste form to incorporate MOF, gas (eg., iodine) and additional components into matrix with no adverse environmental effects

- *Addition of Ag metal to composition to capture any gas liberated during waste form processing (in-situ formation of AgI)*

- Targeted waste form:

✓ compact and monolithic

✓ mechanically, thermally, and chemically stable

✓ able to sustain compatibility with various repository conditions

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Bi-Zn-oxide Based Low-Temperature Sintering Glasses

Bismuth known affinity for Iodine

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

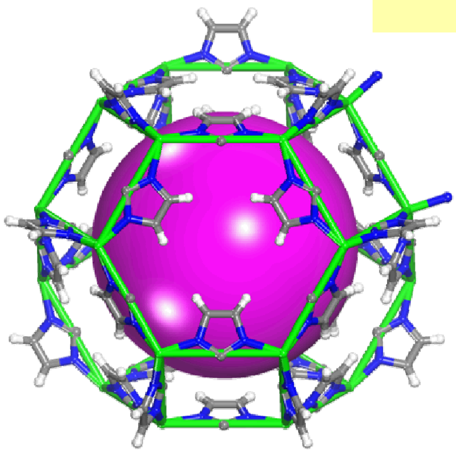
Glass characteristics	**EG2998 (c)**	**EG2922 (a)**
Composition	Bi-Zn-B	Bi-Zn-Si
Firing temperature	500°C	525°C−550°C
Crystallinity	Crystallizing	Vitreous - Amorphous
Density	5.65 g cc^{-1}	5.8 g cc^{-1}

Glass	ZnO		Bi_2O_3		Al_2O_3		B_2O_3		SiO_2	
	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %	mole %	wt. %
EG 2922	14.2	7.8	20.2	63.4	57.8	23.4	7.8	5.4		
EG 2998	49.7	26.9	18.9	58.6					31.3	14.5

Invited Article, special issue: Nuclear Energy
Ind. Eng. Chem. Res., **2011**, in press

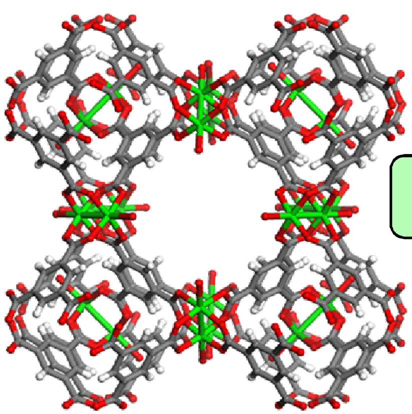
Glass Composite Materials (GCM) Waste Forms

Utilize High Surface Area of MOFs with Selectivity (of Pore Opening or Metal Center)



I_2@ZIF-8 ~ 125 wt.% I_2 +

- EG 2998, Ag → (500 C, 1hr) GCM-1 (c)
- EG 2922, Ag → (525 C, 1hr) GCM-2 (a)



I_2@HKUST-1 ~ 150 wt.% I_2 +

- EG 2998, Ag → (500 C, 1hr) GCM-3 (c)
- EG 2922, Ag → (525 C, 1hr) GCM-4 (a)

80 wt.% glass, 10 wt. % I_2@MOF, 10 wt% Ag

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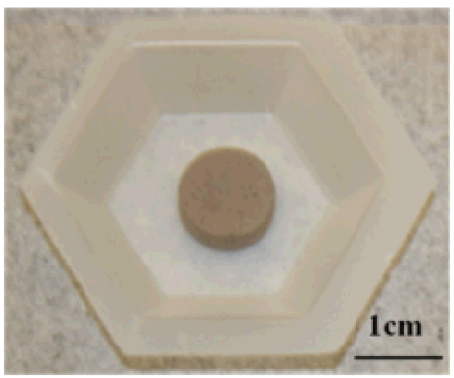
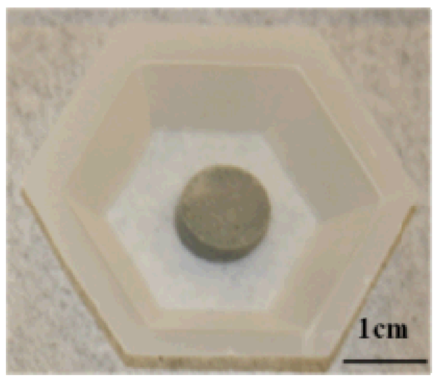
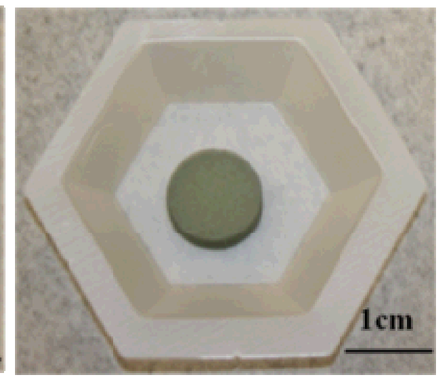
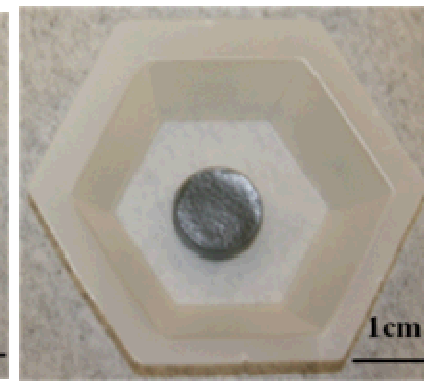
Glass Composite Materials (GCM) Waste Forms – Pressed Pellets

- The powders were homogeneously mixed in a mortar and pestle
- Bulk samples of approximately 2.5 g and 1.2 cm in diameter were pelleted in a binder-free process, by applying a uniaxial mechanical pressure of 70MPa in a steel die



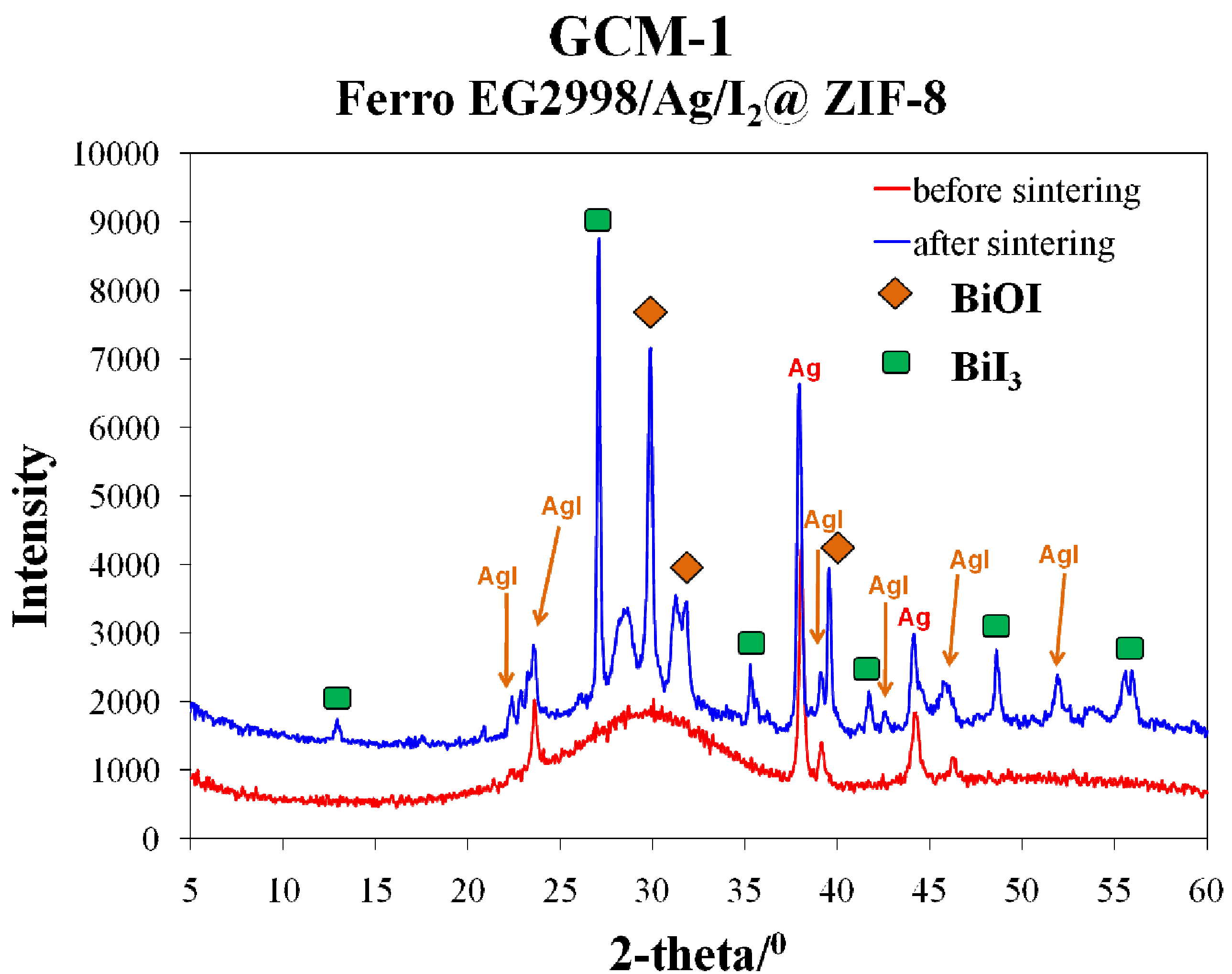






GCM-1	GCM-2	GCM-3	GCM-4
Crystalline	Amorphous	Crystalline	Amorphous
ZIF-8		HKUST-1	

Powder X-ray Diffraction Pattern for GCM-1 Before and After Thermal Treatment (500°C)



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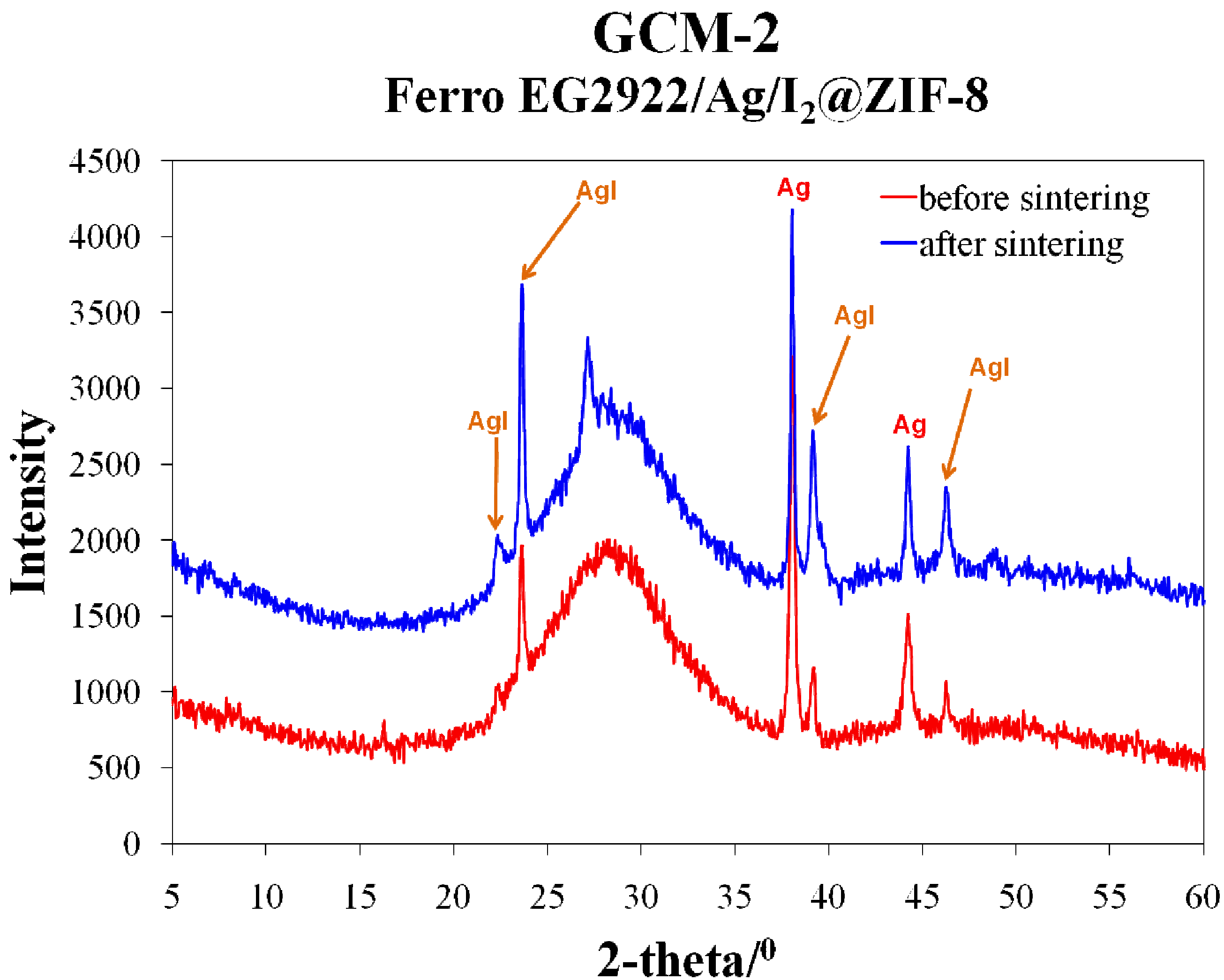
Powder X-ray Diffraction Pattern for GCM-2 Before and After Thermal Treatment (525°C)



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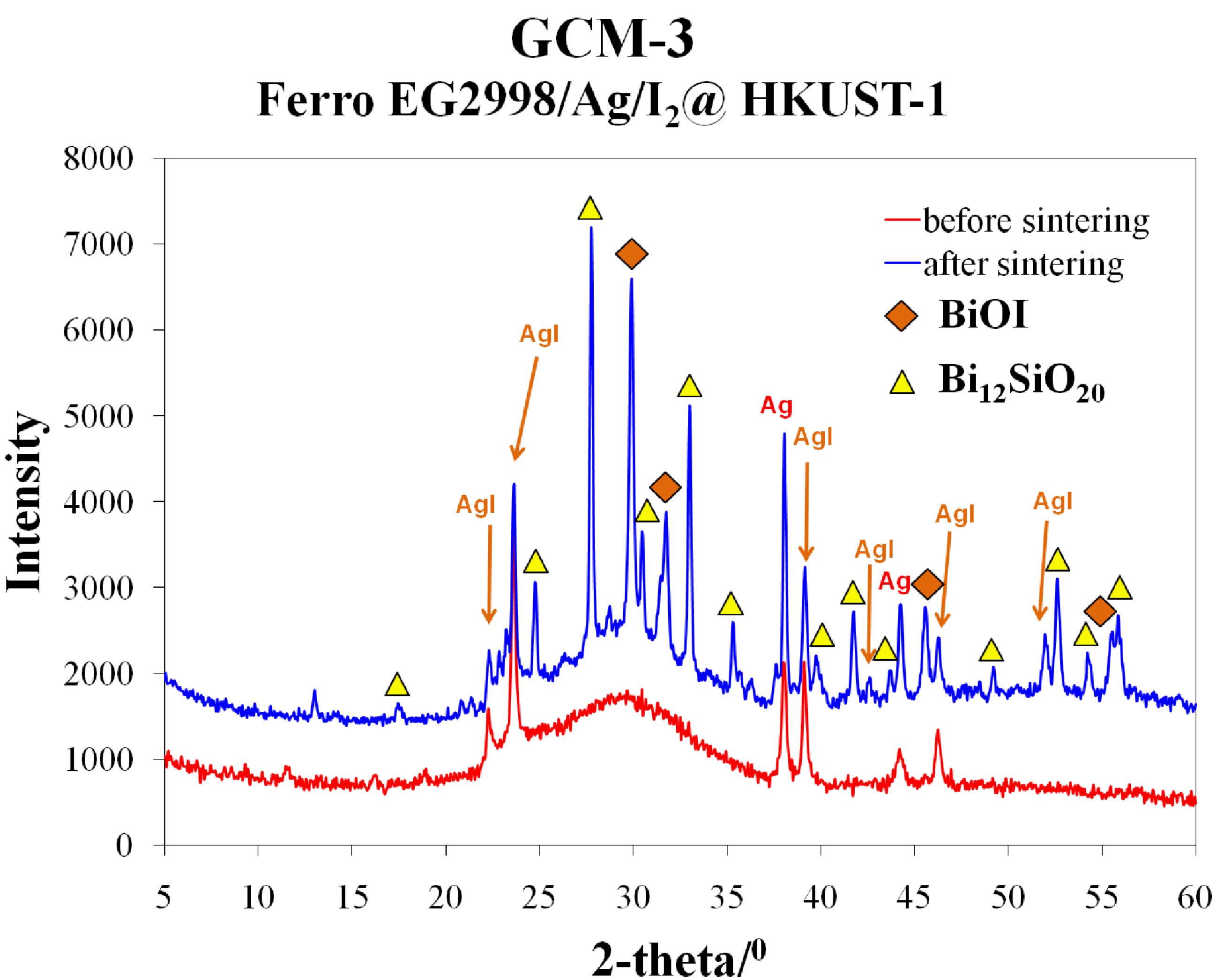
Powder X-ray Diffraction Pattern for GCM-3 Before and After Thermal Treatment (500°C)



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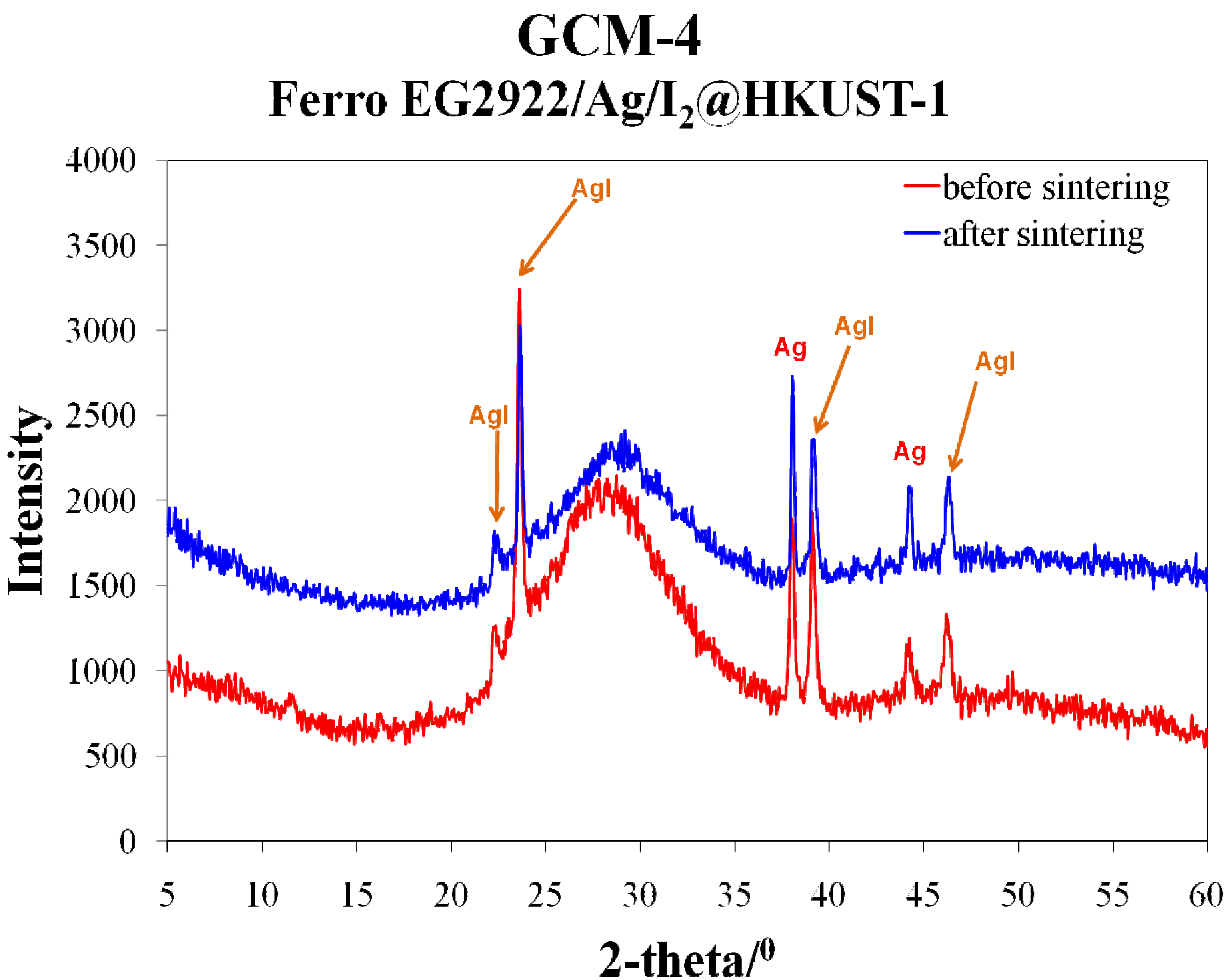
Powder X-ray Diffraction Pattern for GCM-4 Before and After Thermal Treatment (525°C)



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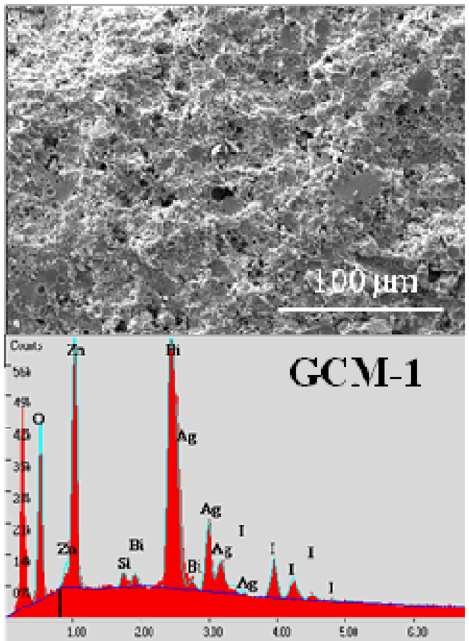
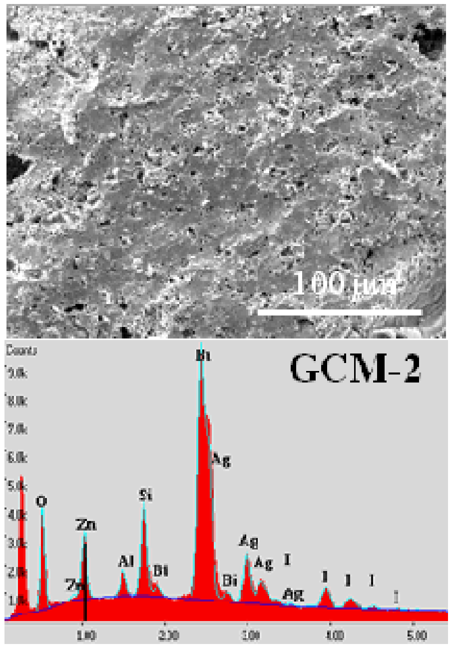
SEM-EDS Spectra of the Sintered GCM pellets
(EDS at Full Field of View)



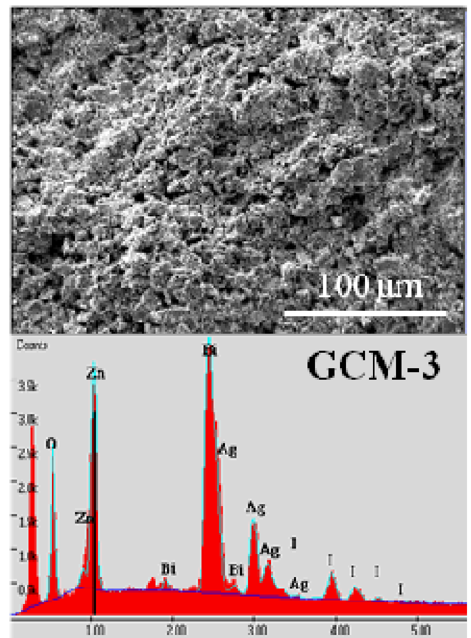


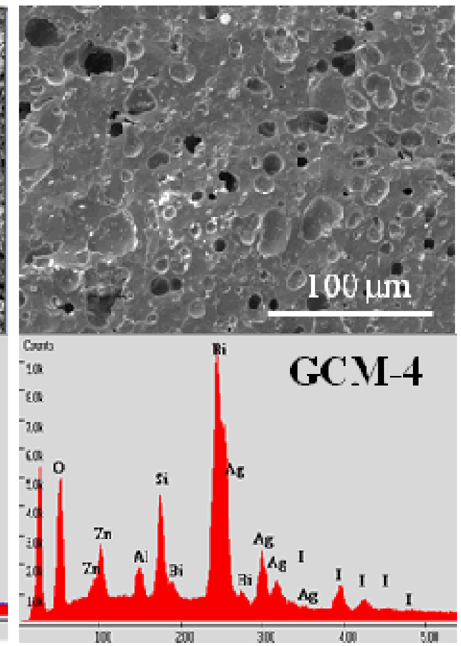
Crystalline Amorphous

ZIF-8

HKUST-1

Crystalline Amorphous





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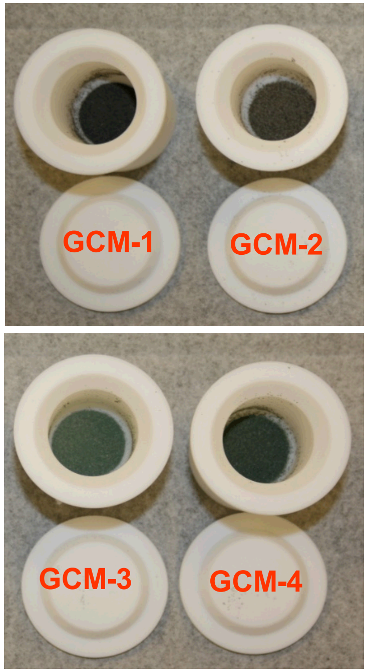
Product Consistency Test (PCT): Leach Durability Results

Standard PCT* test conditions:

1 g of GCM (particle size = 150 -250 μm) in 10mL of DI water at 90°C, 7 days

	GCM-1	GCM-2	GCM-3	GCM-4
B	113	3.1	109	0.5
Na	441	2.1	546	1.8
Si	2.2	2.2	0.8	1.1
K	1	3.6	1.3	2.7
Zn	0	0.05	0	0.5
Ag	0.02	0	0.02	0.2
I	97	0.2	0	0
Bi	0.09	0.01	0.05	0.17



*ASTM Test Designation: C 1285 – 02, ASTM Int., West Conshohocken, PA, 2008

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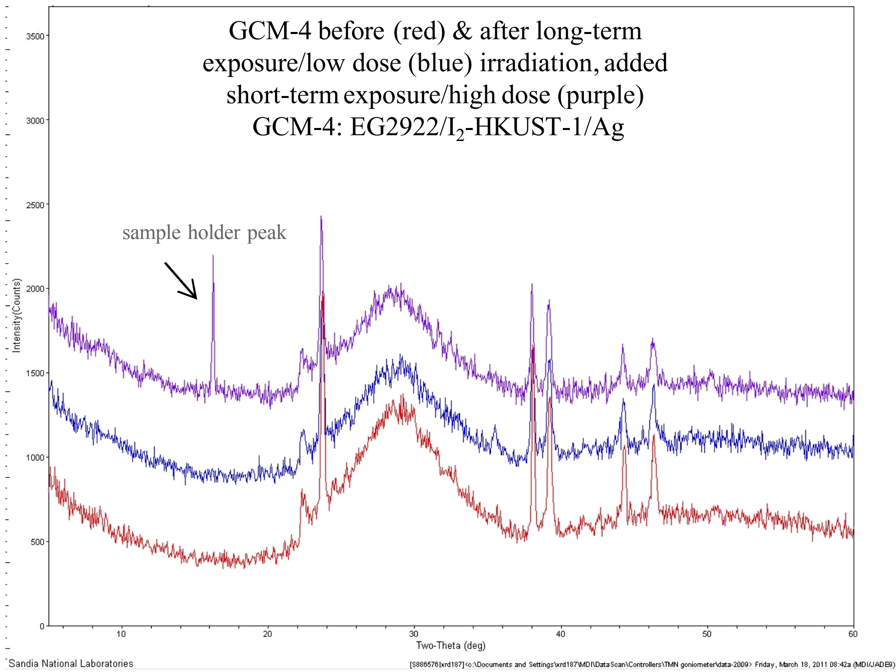
Waste Form Robustness Under Irradiating Conditions - Preliminary Studies



GIF: ^{60}Co source :1.345 x 10^5 Ci

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.*

Total dose: 1.3 x 10^6 Rads; Dose rates:

long-term exposure/low dose: 0.1 Rads/sec, 2.59 x 10^5 Rads (2218Gy)

short-term exposure/high dose: 800 Rads/sec, 1 x 10^6 Rads (10,000 Gy)

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*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).

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Summary and Future directions

- Metal-Organic Frameworks were implemented for the first time as high-capacity I_2 adsorbents (see Sava, etal., Thursday, 1:45pm, UU12.2)
- The I_2-loaded MOFs were successfully encapsulated into stable waste forms
- Novel Glass-Composite-Materials (GCM) have been developed and characterized for long-term storage (for the first time utilizing MOFs as getter materials)
- GCMs reveal excellent thermal and chemical stability; *no iodine is lost during processing or after undergoing leach durability studies*
- Ongoing studies:

  glass composition optimization

  comprehensive studies of GCMs under irradiating conditions

  In-situ Mechanism studies of Ag Clusters within Zeolites

  (see Zhao, etal., Friday, 4:15pm, FF16.8)

Gordon Research Conferences

frontiers of science

http://www.grc.org/programs.aspx?year=2011&program=nanopor

Conference Program

Nanoporous Materials & Their Applications

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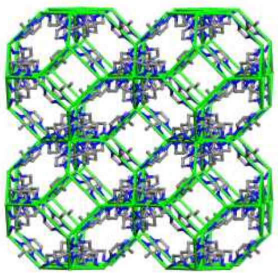
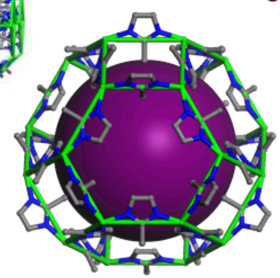
July 10, 2011

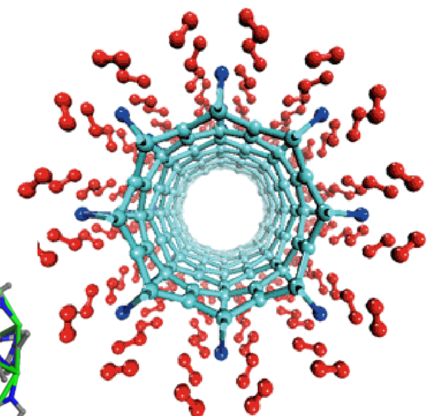
August 7-12, 2011
Holderness School
Holderness, NH USA

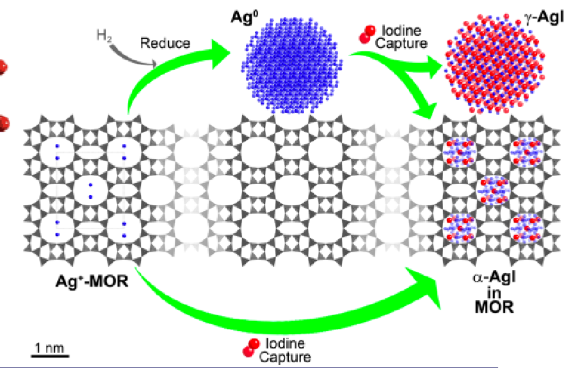
Chair:
Tina M. Nenoff,
Sandia National Labs

Vice Chair:
Yushan Yan, UC Riverside









Confirmed Speakers and Discussion Leaders:

* Avelino Corma, Valencia Polytechnic University, Spain
* Omar Yaghi, UCLA
* Valentin Valtchev, ENSICAEN / Université de Caen
* Debra Rolison, Naval Research Laboratory
* Karl Strohmaier, ExxonMobil
* Berend Smit, UC Berkeley
* Karena Chapman, Argonne National Laboratory & APS
* Mark Allendorf, Sandia National Laboratories/CA
* Junlan Wang, University of Washington
* Joseph Hupp, Nortwestern University
* Herve Jobic, University of Lyon & CNRS, France
* C. Jeffrey Brinker, Sandia National Laboratories/NM
* Susannah Scott, UC Santa Barbara
* Bruce Gates, UC Davis
* Sankar Nair, GA Tech University
* Jing Li, Rutgers University
* Guillaume Maurin, Université Montpellier
* Andrew I. Cooper, Univ. Liverpool, UK

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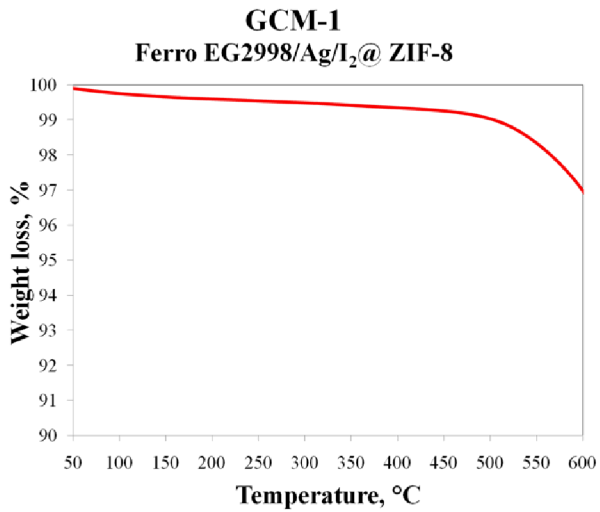
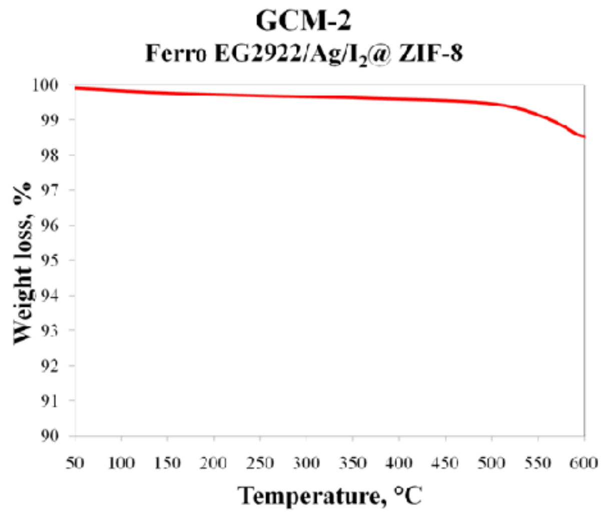
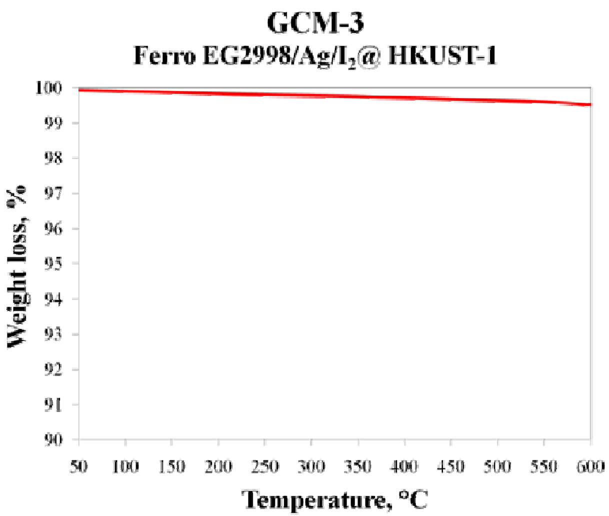
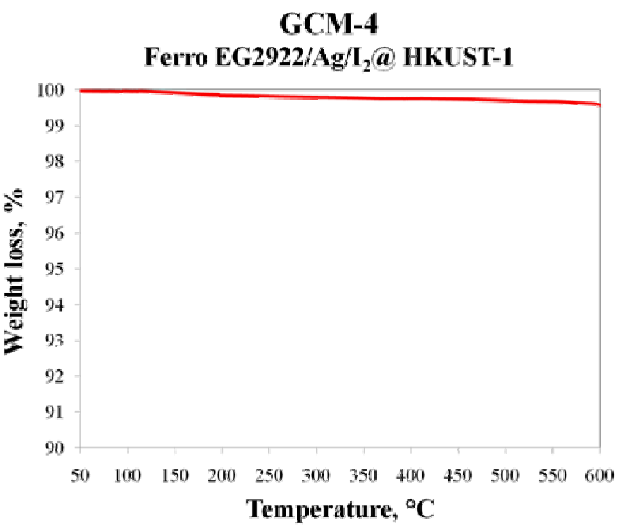
Additional Slides

Thermogravimetric analysis of the simulated waste forms series









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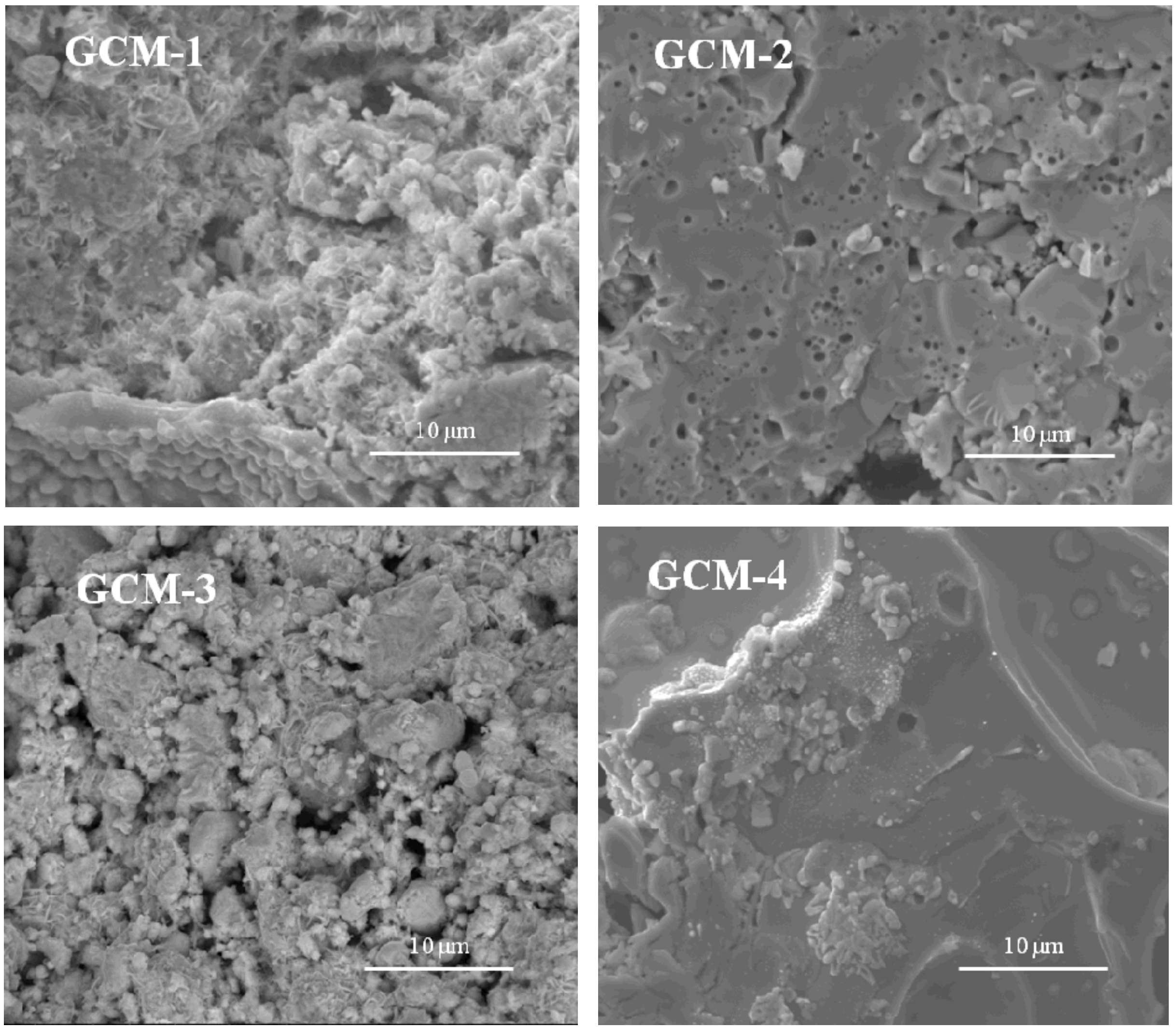
SEM micrographs of zoomed-in regions in the sintered GCM series



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