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Sandia National Laboratories

SAND2015-7244C

The Fuel Cycle Research & Development

Low Temperature Glass Composite Material (GCM) Waste Form for Radiological Iodine Captured by Ag-Zeolites: Optimization and Durability

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Global2015, Paris, France
Sept 24, 2015

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Outline

I. Introduction
II. Bi-Si-Zn Oxide Glass for Glass Composite Materials Waste Form
III. GCM Synthesis Variables vs. Durability
   a. Weight % level of AgI-MOR in GCM
   b. Particle Size of AgI-MOR in GCM
   c. GCM Sintering
IV. Conclusions

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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:

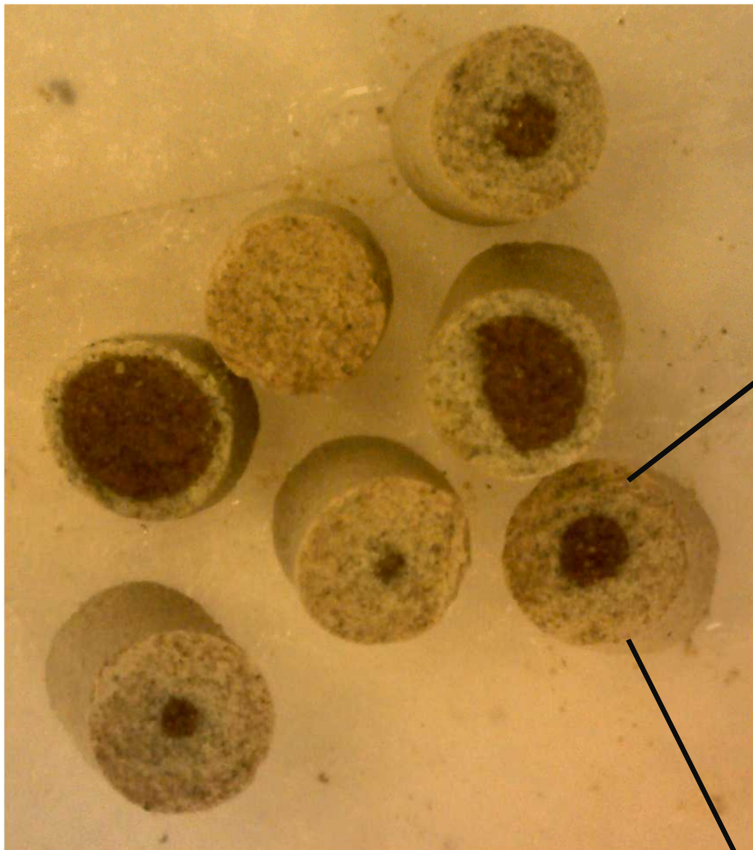
✓ compact and monolithic

✓ 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

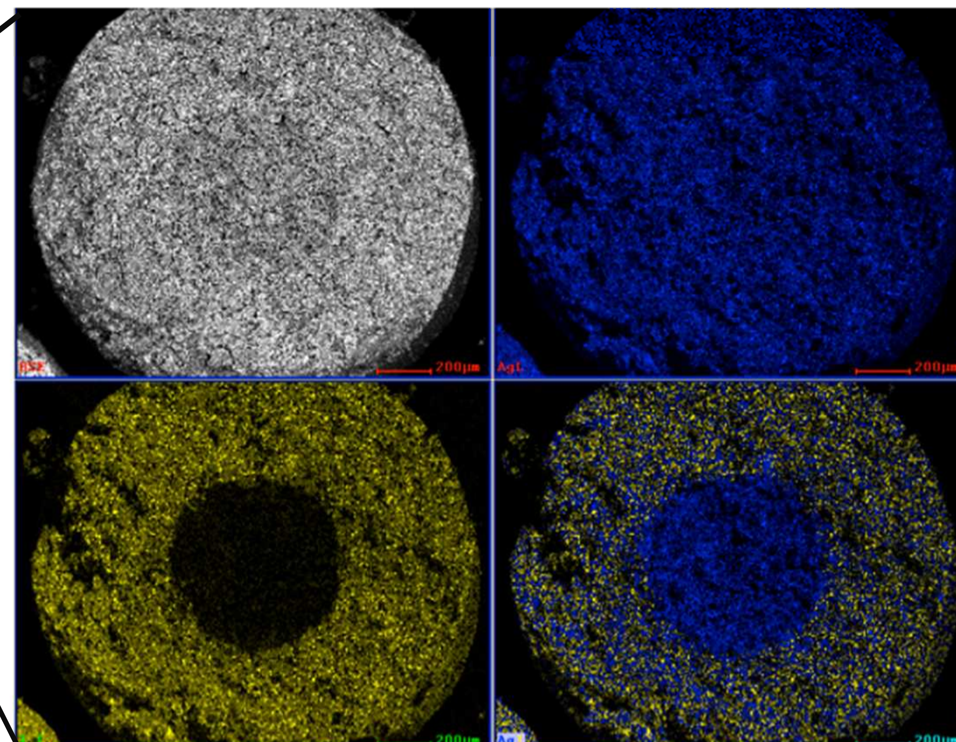
Example of loaded AgI-zeolite to be Encapsulated in Waste Form



“as received” AgI-MOR from ORNL, for INL CH_3-I Deep Bed Studies

SEM-EDS, yellow = I, blue = Ag

ORNL AgI-MOR As-Received Pellet in Cross-Section



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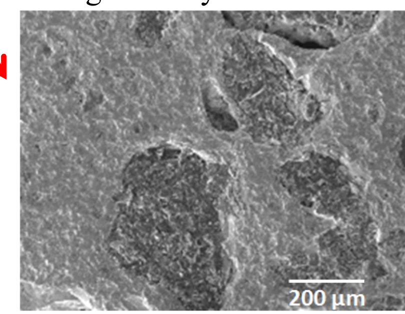
GCM Bi-Zn Oxide Low-Temperature Sintering Glasses

Glass characteristics	*EG2998	*EG2922
Composition	Bi-Zn-B	Bi-Zn-Si
Sintering temperature	500°C	525°C–550°C
Crystallinity	Crystallizing	Vitreous
Density	5.65 g cc^{-1}	5.8 g cc^{-1}

*purchased from Ferro Corporation

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



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

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Glass Composite Material (GCM) Waste Form

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.

US Patent 8,262,950; **2012**

**PCT: The Product Consistency Test (PCT), designation: C 1285 – 02. ASTM Int., West Conshohocken, PA, 2008.

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

Durability Testing: Elucidation of Degradation Mechanisms in loaded GCM

Mowry, C.D.; Brady, P.V.; Garino, T.J.; Nenoff, T.M.
"Development and Durability Testing of a Low Temperature Sintering Bi-Si-Zn Oxide Glass Composite Material (GCM) ^{129}I Waste Form"
J. Amer. Ceram. Soc., **2015**, in press, DOI: 10.1111/jace.13751; and references within

Data indicates that:

- The Bi–Si–Zn oxide glass matrix dissolves at a relatively low rate;

- The Bi–Si–Zn oxide glass matrix limits the release of iodine from the otherwise relatively fast degrading (as-received) AgI-MOR getter material;

-The formation of an amorphous AgI phase results in the limitation of iodine release.

- Durability of GCM and release rates approximate those of established nuclear waste glasses, or analogues such as basaltic glass. *This suggests that the Bi–Si–Zn GCM is a viable candidate as a repository iodine waste form*.

Durability Testing: PCT, MCC-1, SPFT

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

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

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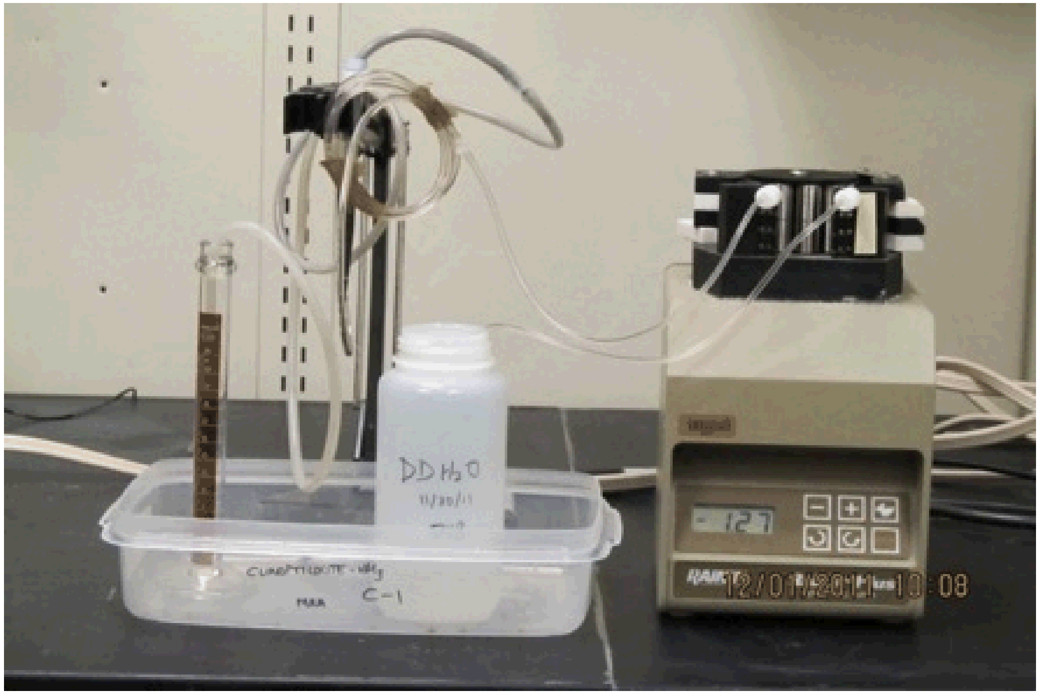
For SPFT*, for AgI-GCM:
Ground to ~ 3 microns (glass)
0.1 - 1 grams in 2 ml vol reactor
Surface area = 2.6 (glass), 21 (AgI-MOR) m^2/g
Temps: 25 and 60^oC
pH: 3.3 – 7.5
Test solutions pumped:
220 – 340 ml/day (2.5 – 3.9 x 10^{-7} L/s)

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

*Chou and Wollast (1985; American Journal of Science)



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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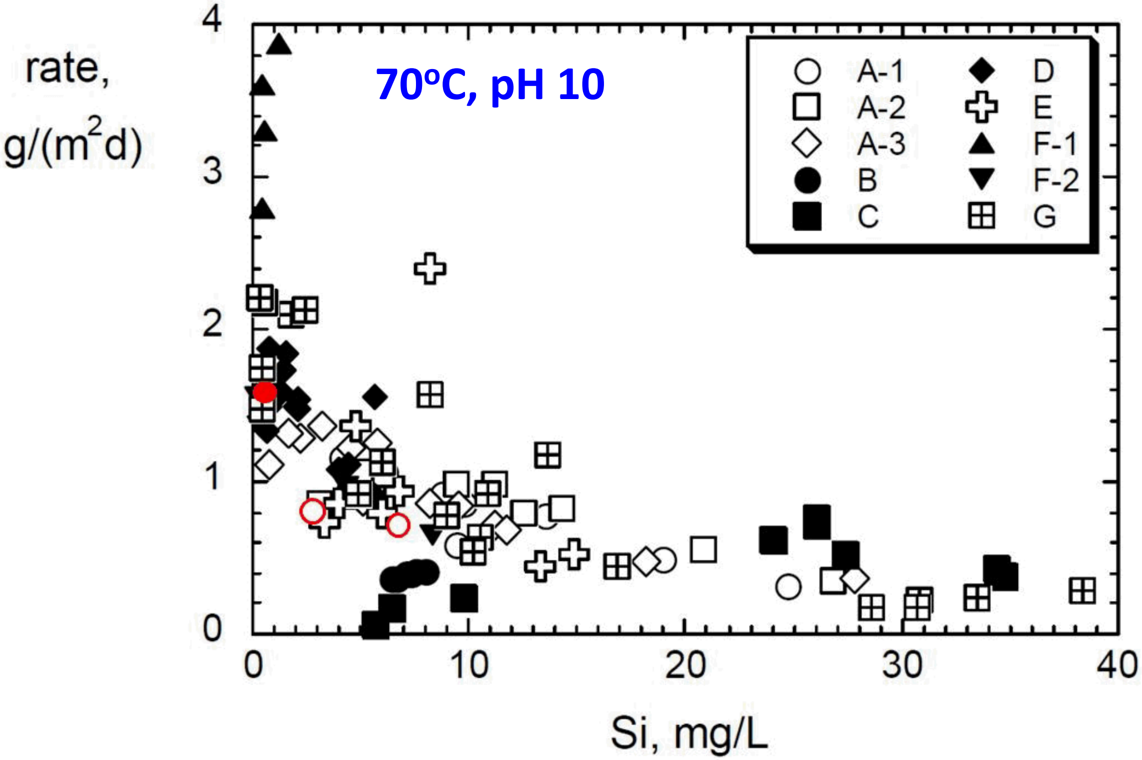
Benchmark SPFT Method Against LRM Glass Results

Steady-state LRM Glass Degradation Rates



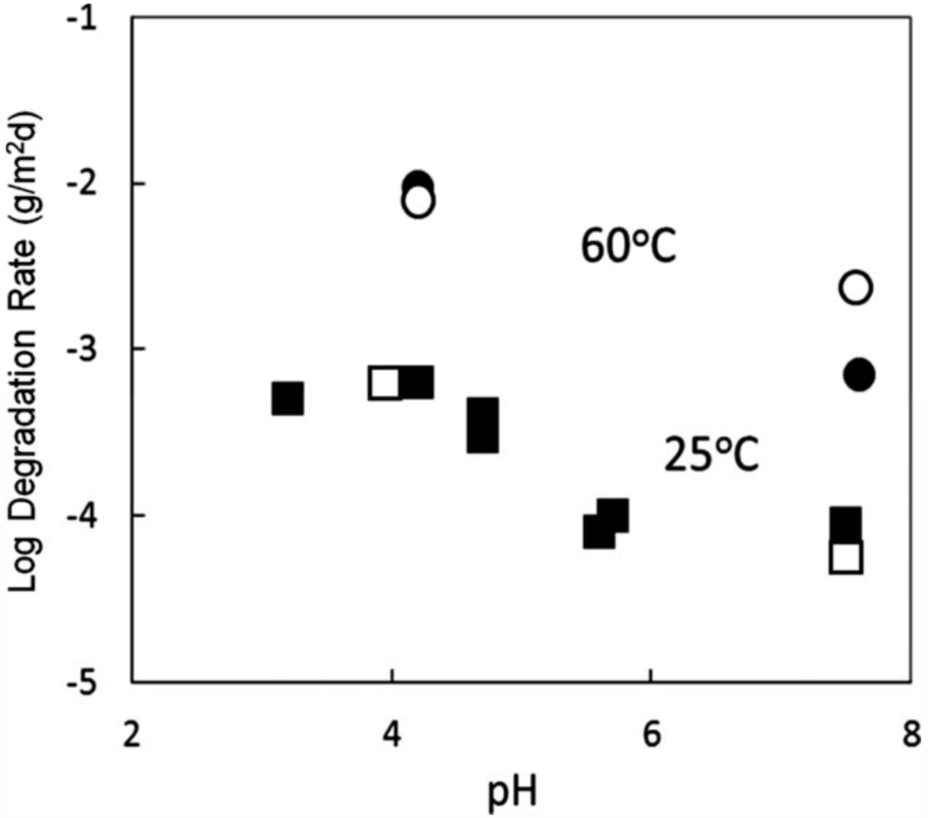
LRM glass surface area = 0.021 m^2/g (0.2 g); Input solution - 0.004 molal LiCl/0.003 molal LiOH; q/S = 3.1 x 10^{-7}, 9.0 x 10^{-7}, and 1.0 x 10^{-5} m/s; effluent Si - 0.3 to 7 ppm.

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 70ºC 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

Degradation Rates of Bi-Si-Zn Oxide Glass



pH- and temperature-dependent degradation rates of Bi-Si-Zn oxide glass (filled symbols) at 25 (squares) and 60°C (circles), calculated from silica release in SPFT testing.

Unfilled symbols are literature values* for CSG glass at 25°C and interpolated values at 60°C. (*Knauss, et.al, *MRS Symp. Proc*. **1990**, *176*, 371)

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

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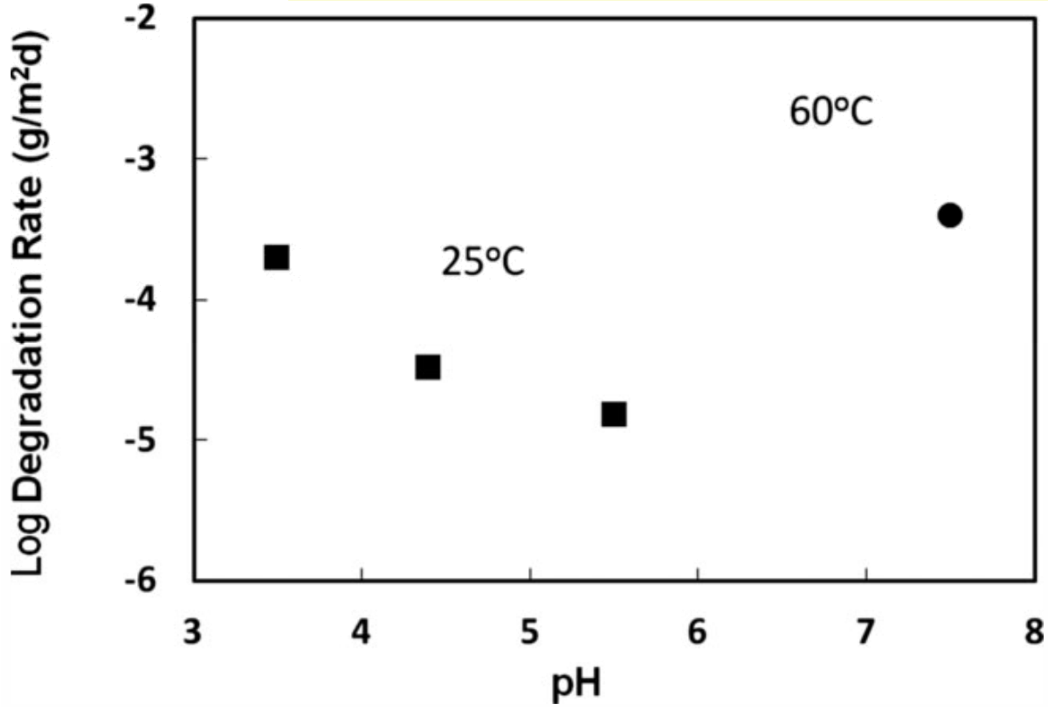
Degradation Rates of AgI-MOR: *Slower than glass degradation*

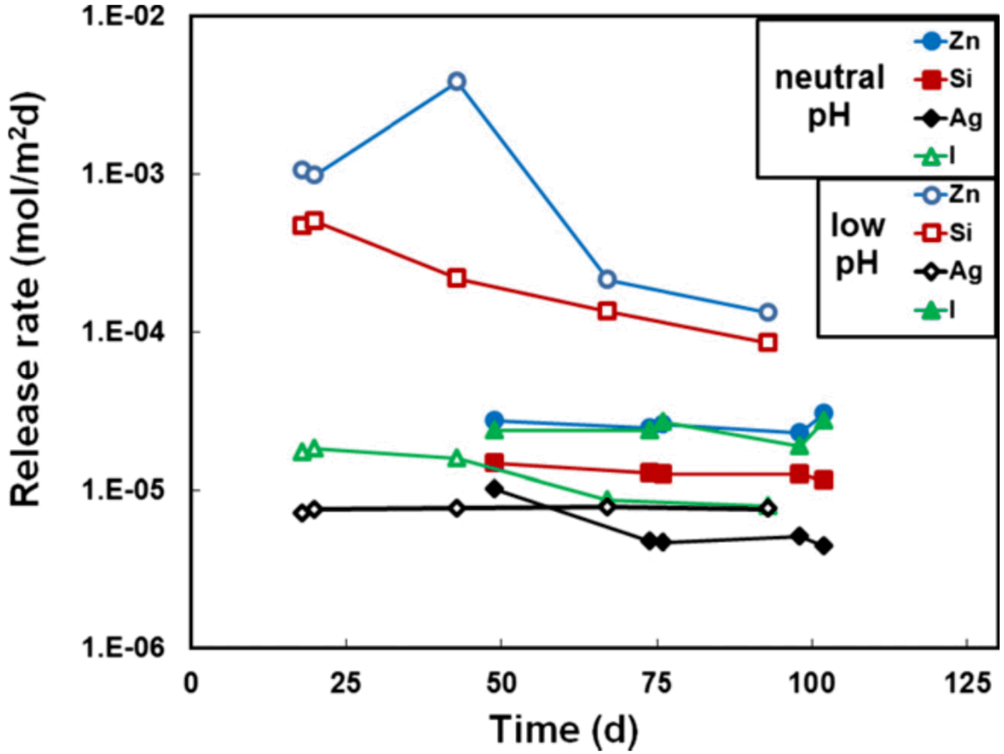
Degradation of AgI-MOR at 25°C (squares) and 60°C (circles) calculated from silica release in SPFT testing.



Si and Zn release occurred far from equilibrium but did not reach steady state.

- Release of both elements increases with decreasing pH.
- Concentration of Zn and Si released increased by a factor of 12 – 20, from pH 6.5 - 2.5.\
- Alteration phase formations - Eulytite ($Bi_4(SiO_4)_3$)

Degradation Rates of GCM Components: Molar Release Rates at variable pH



Molar release rates of GCM components for representative pH ~2.3 (open symbols) and pH ~6.6 (filled symbols) SPFT runs. Zn – red; Si – blue; Ag – black; I – green.

- Low & near neutral: Zn releases faster than Si
- Low pH: both Zn and Si release more rapidly than Ag and I.
- Ag and I in effluent levels were similar at each pH and for each I loading.
- Steady-state I effluent levels ranged from 3 – 12 ppb.

There is no strong link between durability (dissolution) and Iodine loading.

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AgI-MOR wt% Loading Levels Effect on GCM Durability

Utilizing ORNL AgI-MOR with 8.7 wt% I_2

Two GCM samples synthesized with greater wt % AgI-MOR than SNL baseline tests (20 wt %):
22 wt % AgI-MOR in GCM (78 wt% glass)
25 wt % AgI-MOR in GCM (75wt% glass)

Glass (density of 5.8 g/cm^3),
1.1% Ag flake for 20 wt % AgI-MOR sample,
1.21 % Ag flake for the 22 wt % sample, and
1.375% Ag flake for the 25 wt % sample
} to maintain Ag flake : AgI-MOR ratio

Sintered 550 °C, 1 hr.
GCM samples ground to < 38 µm
BET surface areas of sintered GCM = 3.43 m^2/g, 6.4m^2/g respectively

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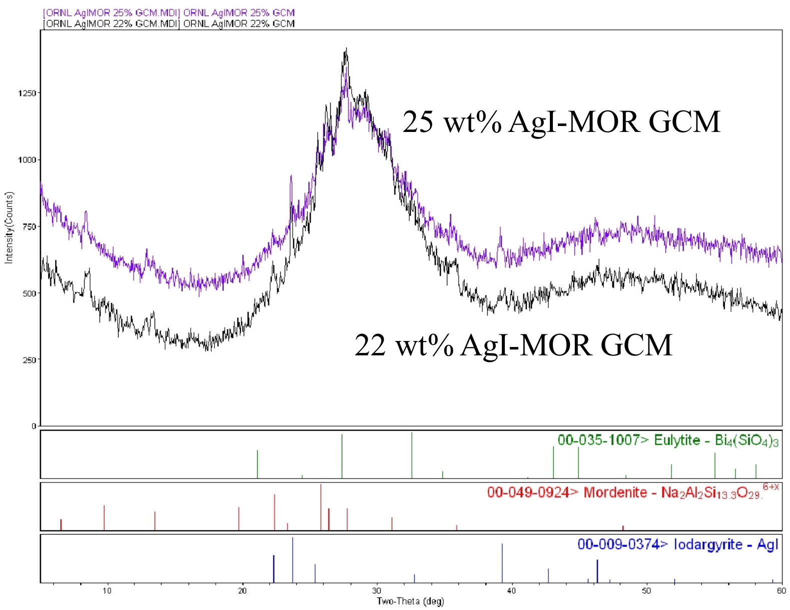
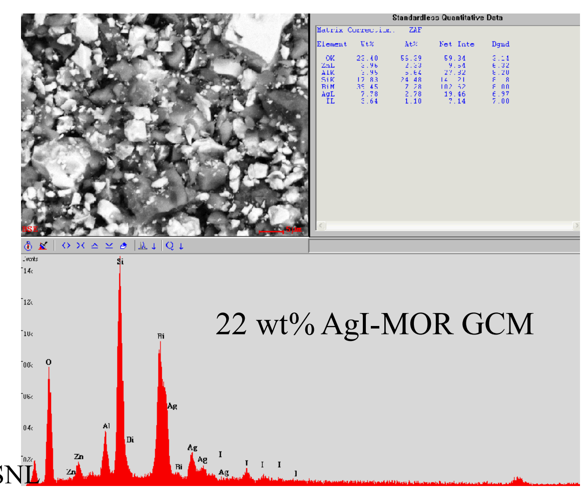
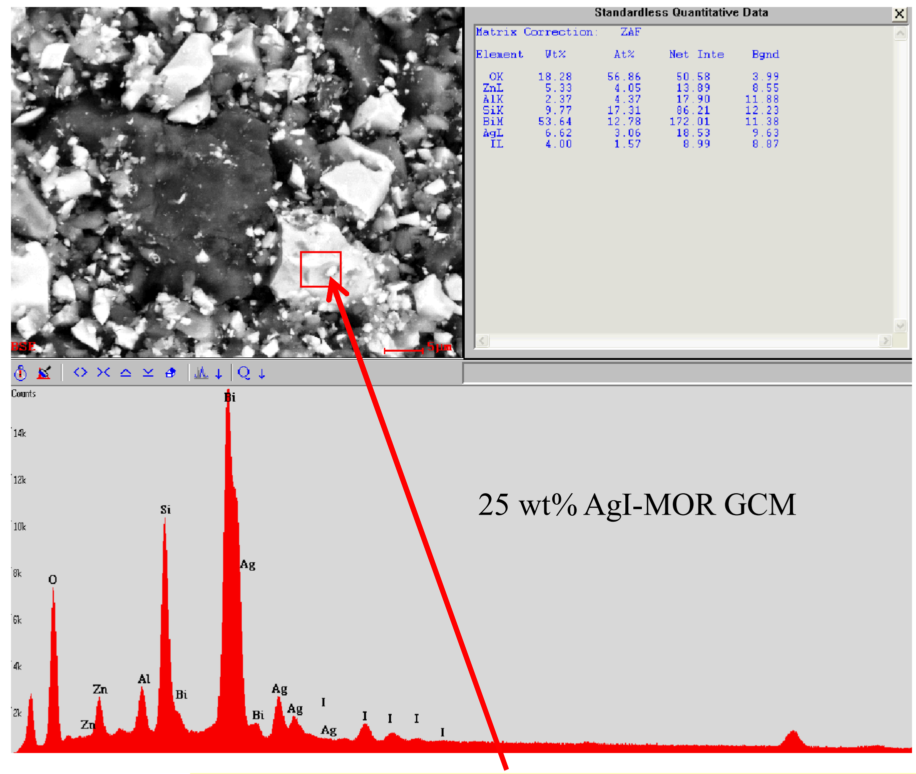
AgI MOR Wt% Loading Levels Effect on GCM Durability

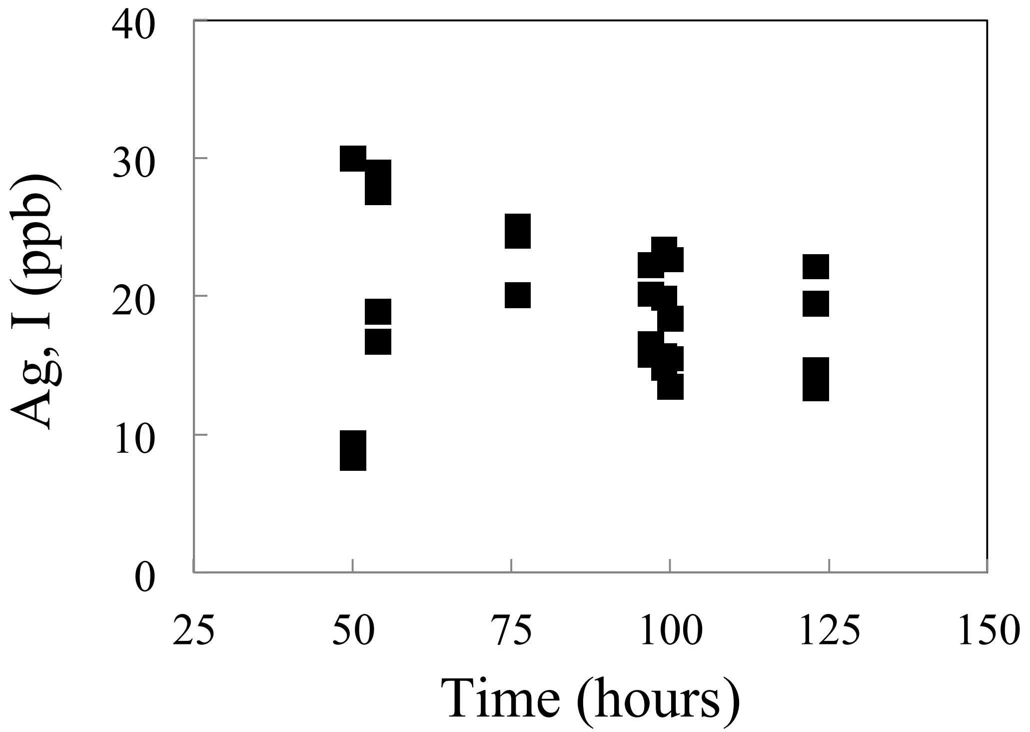






Focused/point EDS indicates majority of AgI located in brightly colored silicon rich crystallites

AgI MOR wt% Loading Levels Effect on GCM Durability



Ag (unfilled symbols) and I (filled symbols) effluent levels as a function of time. Circles = 22% AgI-MOR; triangles = 25% AgI-MOR.

GCM durability is independent of AgI-MOR wt % loading

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AgI MOR Particle Size Effect on GCM Durability

Utilizing ORNL AgI-MOR with 8.7 wt% I_2

GCM samples synthesized with three AgI-MOR particle sizes:

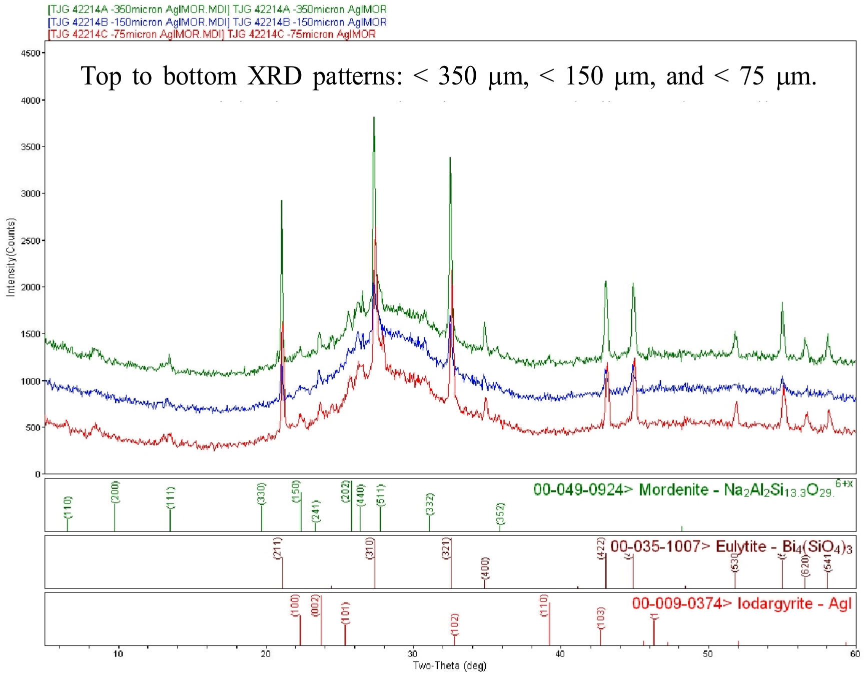
- < 350 µm
- < 150 µm
- < 75 µm

Baseline particle size in earlier studies <150 µm

GCM: 20 wt % AgI-MOR + 80 wt% Glass + 1.1 wt% Ag flake

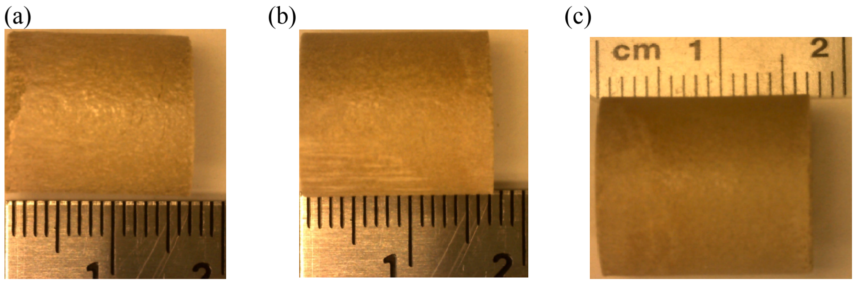
Sintered 550 °C, at 5°C/min, 1 hr.
GCM samples ground to < 38 mm
BET surface areas of sintered GCM = 3.45 m^2/g, 2.94 m^2/g, and 3.61 m^2/g, respectively

AgI MOR Particle Size Effect on GCM Durability

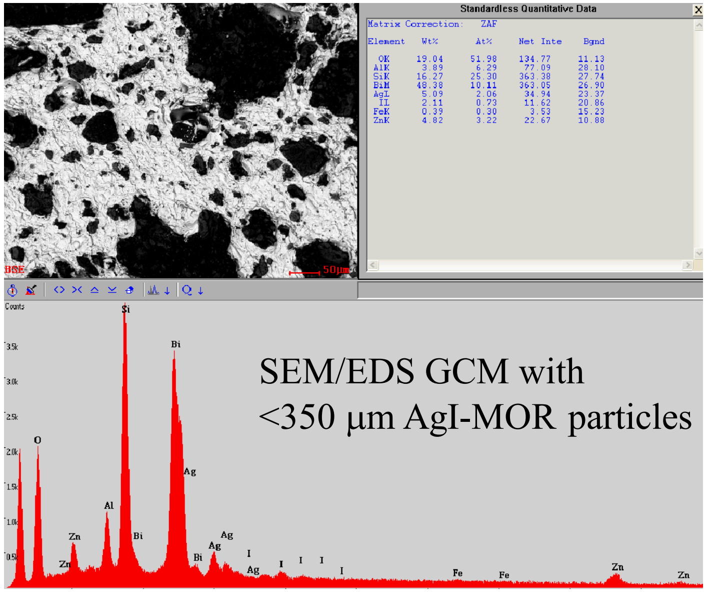


<150 μm has smallest quantity Eulytite.
Further study required as to why it forms

Bulk Morphology does not change with particle size



< 350 μm, < 150 μm, and < 75 μm.



SEM/EDS GCM with
<350 μm AgI-MOR particles

Reflective of other samples

AgI MOR Particle Size Effect on GCM Durability

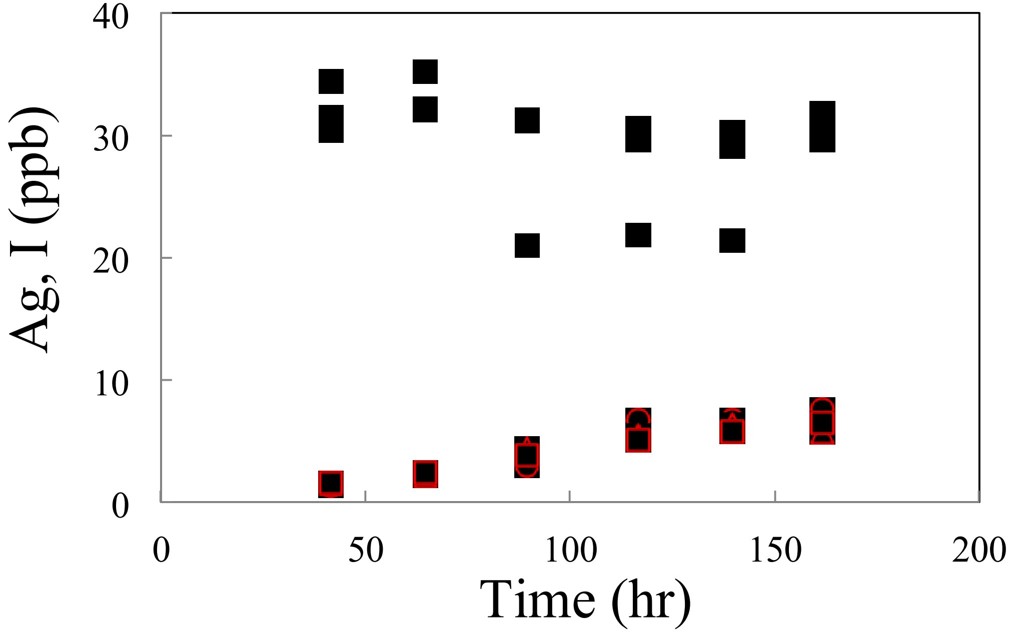


Figure 1: Ag (unfilled symbols) and I (filled symbols) effluent levels as a function of time. Circles are for d < 350 µm runs; squares are d < 150 µm runs; triangles are d < 75 µm runs.

- AgI-MOR particle size in GCM has no effect on iodine or silver release
- Both are limited by the low solubility of AgI

Higher Ag relative to I in effluent suggests Ag leaching from GCM controls equilibrium levels of iodine

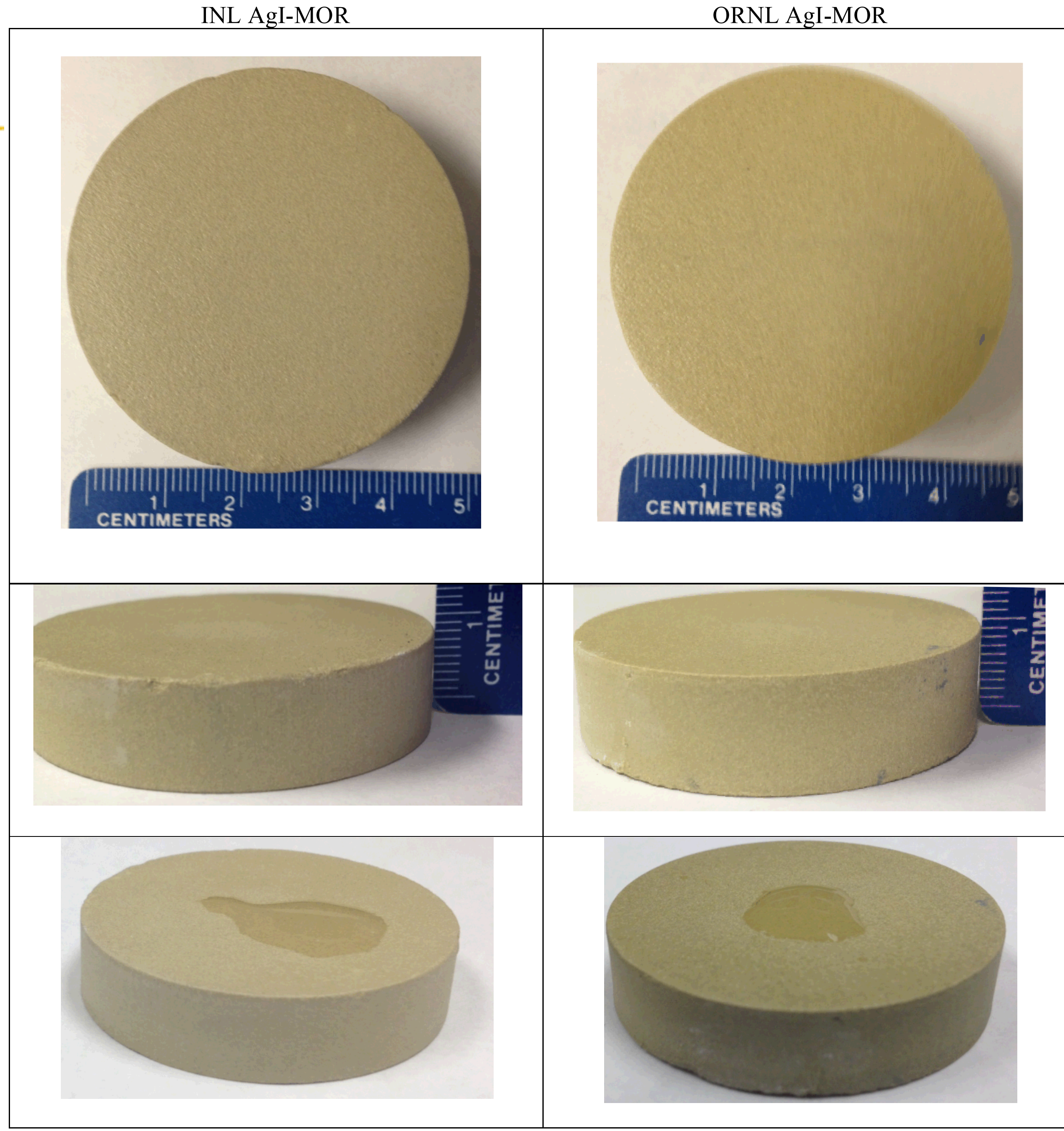
GCM 2.0: Successful Scale-Up

Optical images of fired GCMs.

Left: GCM containing 20wt% INL CH_3I-loaded AgI-MOR.

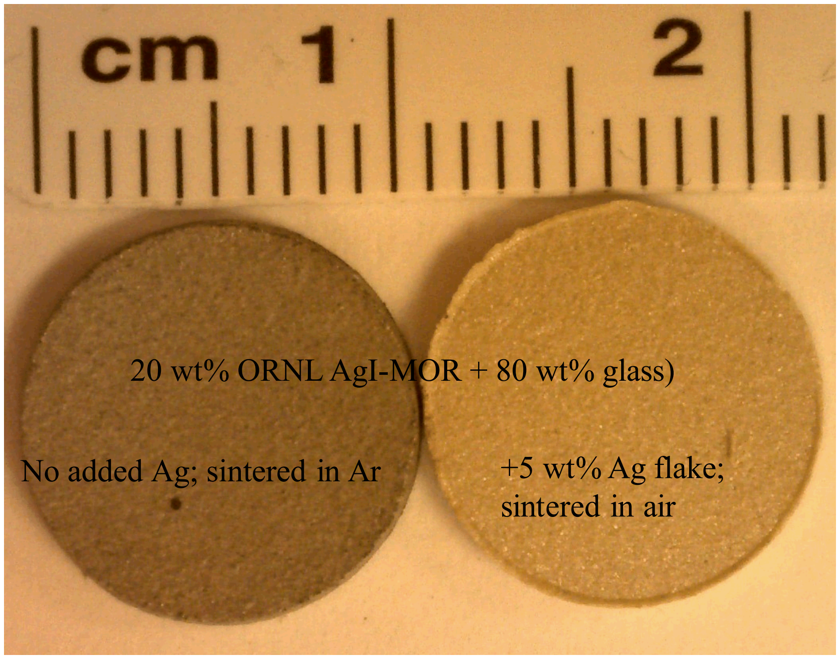
Right: GCM containing 20wt% ORNL I_2-loaded AgI-MOR

Nenoff, et.al., 2015, FCRD-MRWFD-2015-000120

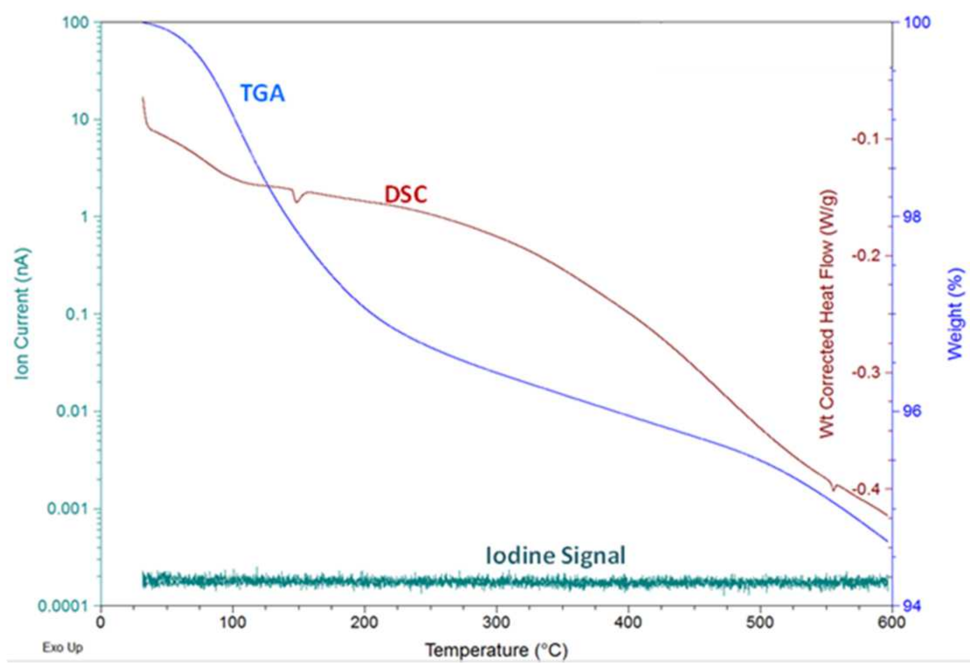


GCM 2.0: Effect of Atmosphere during Sintering on Iodine Retention & GCM

Sintering: 5°C/min to 550°C for 1 hr



Sintering in Inert:
20 wt% ORNL AgI-MOR +
80 wt% glass
No added Ag flake



Preliminary Results, if sintered in inert atm:

1) No need for Ag flake

2) No oxidation of Ag present in AgI-MOR

3) Transport of AgI from bulk into MOR pores (added physical retention of Iodine)

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Durability of GCM and release rates approximate those of established nuclear waste glasses, or analogues such as basaltic glass. *This suggests that the Bi–Si–Zn GCM is a viable candidate as a repository iodine waste form.*

• The Bi–Si–Zn oxide glass matrix dissolves at a relatively low rate. Flow-through testing data indicate low GCM dissolution rates (<10^{-3} g/m^2d) across wide variable ranges including: pH, AgI-MOR loading, I loading, and AgI-MOR particle size;

• The Bi–Si–Zn oxide glass matrix limits the release of iodine from the otherwise relatively fast degrading (as- received) AgI-MOR getter material, by encapsulating and/or reducing leachability through the heat treat- ment used to create the GCM;

•The formation of an amorphous AgI phase results in the limitation of iodine release during waste form degradation.

Uncertainty remains about AgI-MOR dissolution controls; why are Ag and I not limited by amorphous AgI precipitation in the AgI-MOR durability and degradation tests?

Further study of the degradation kinetics associated with amorphous AgI transformation to lower solubility crystalline AgI is necessary.

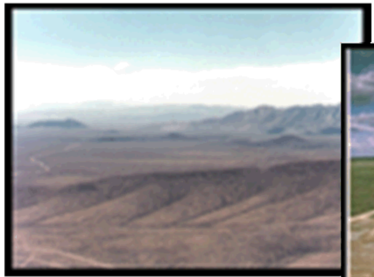
Thank You

Sandia National Laboratories' Sites

Albuquerque, New Mexico

Kauai Test Facility Hawaii

Tonopah Test Range, Nevada



Yucca Mountain, Nevada

WIPP, New Mexico

Pantex, Texas

Livermore,California

Extra Slides

Impact of Results to Date on MRWFD Campaign

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Durability studies to date indicate a waste form that is as stable as known nuclear waste glasses.
Flexible/ Universal waste form, acceptance of many rad-loaded getter materials
Scaleable

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

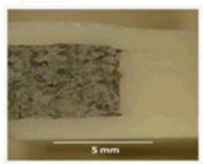
50 wt% AgI/50 wt% Glass
500°C for 3 hr

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

"Universal" Low Temperature Glass Waste Form
Glass Composition (2922), no HIP-ping needed:
Sintering 550° C, Mole % oxides:
32 BiO_3, 19 ZnO, 44 SiO_2, 5Al_2O_3

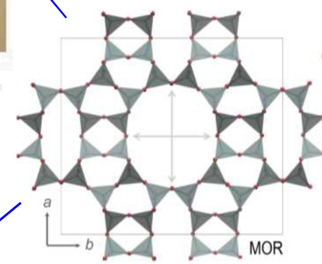
Core-Shell GCM Glass Waste Forms

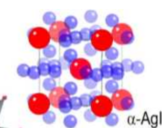
Glass shell, AgI/glass core,
75/25

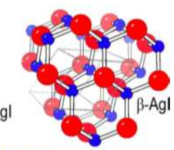


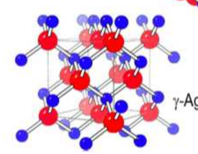
Glass shell,
AgI-MOR/Ag/Glass core 80/20/5

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



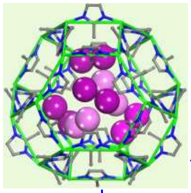


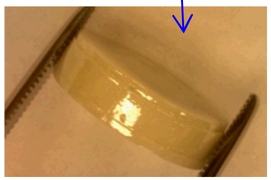




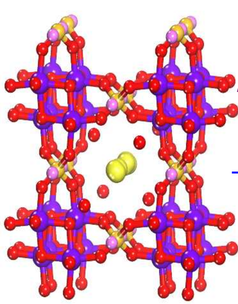
AgI bp 556° C

I_2/MOF, Isolation to Waste Form
JACS, **2011**,*133(32)*,12398
Ind. Eng. Chem. Res (Invited Article*)* **2012**, *51*(2), *614*
US Patent 8,262,950

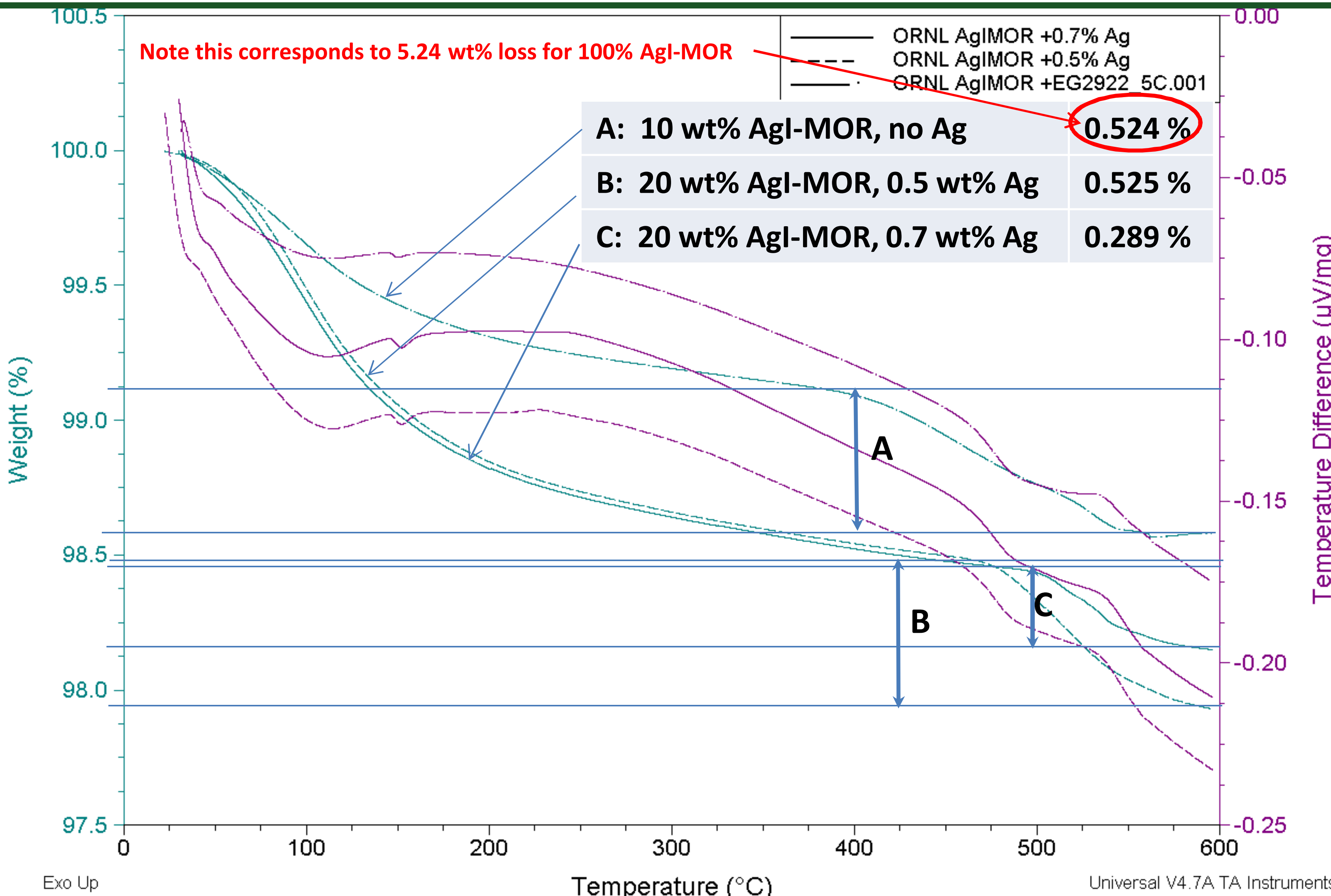




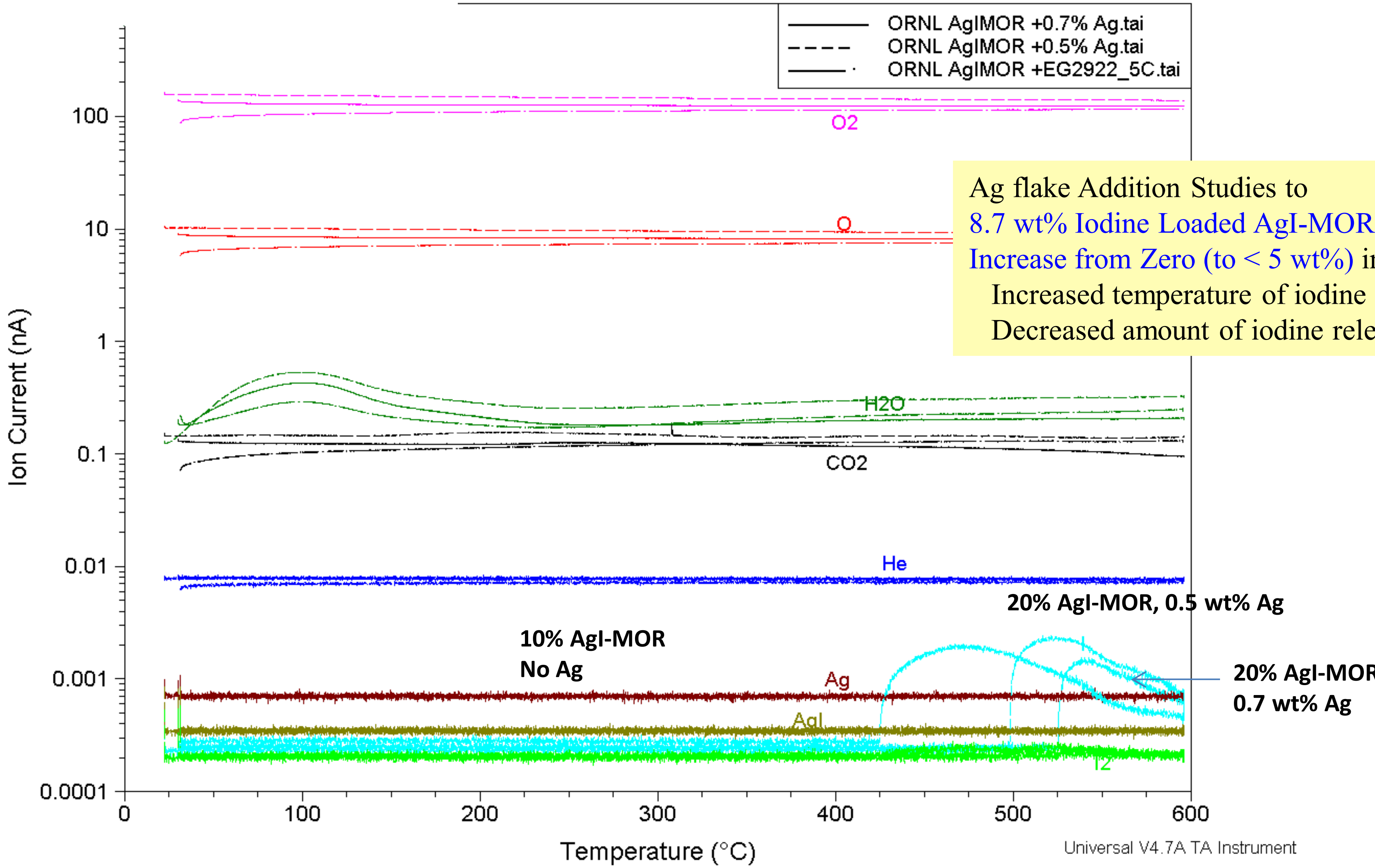
Cs-CST Low Temp Glass Waste Form, No Cs Loss in Sintering
US Patent 8,262,950



Minimization of Ag Flake in GCM



TGA-DTA-MS Data Describe Effect of Ag Flake vs. Iodine Release



Ag flake Addition Studies to
8.7 wt% Iodine Loaded AgI-MOR (ORNL):
Increase from Zero (to < 5 wt%) indicates:
- Increased temperature of iodine release,
- Decreased amount of iodine release.

1.1 wt%: Optimized Ag Flake for Standard (non-optimized) Loadings

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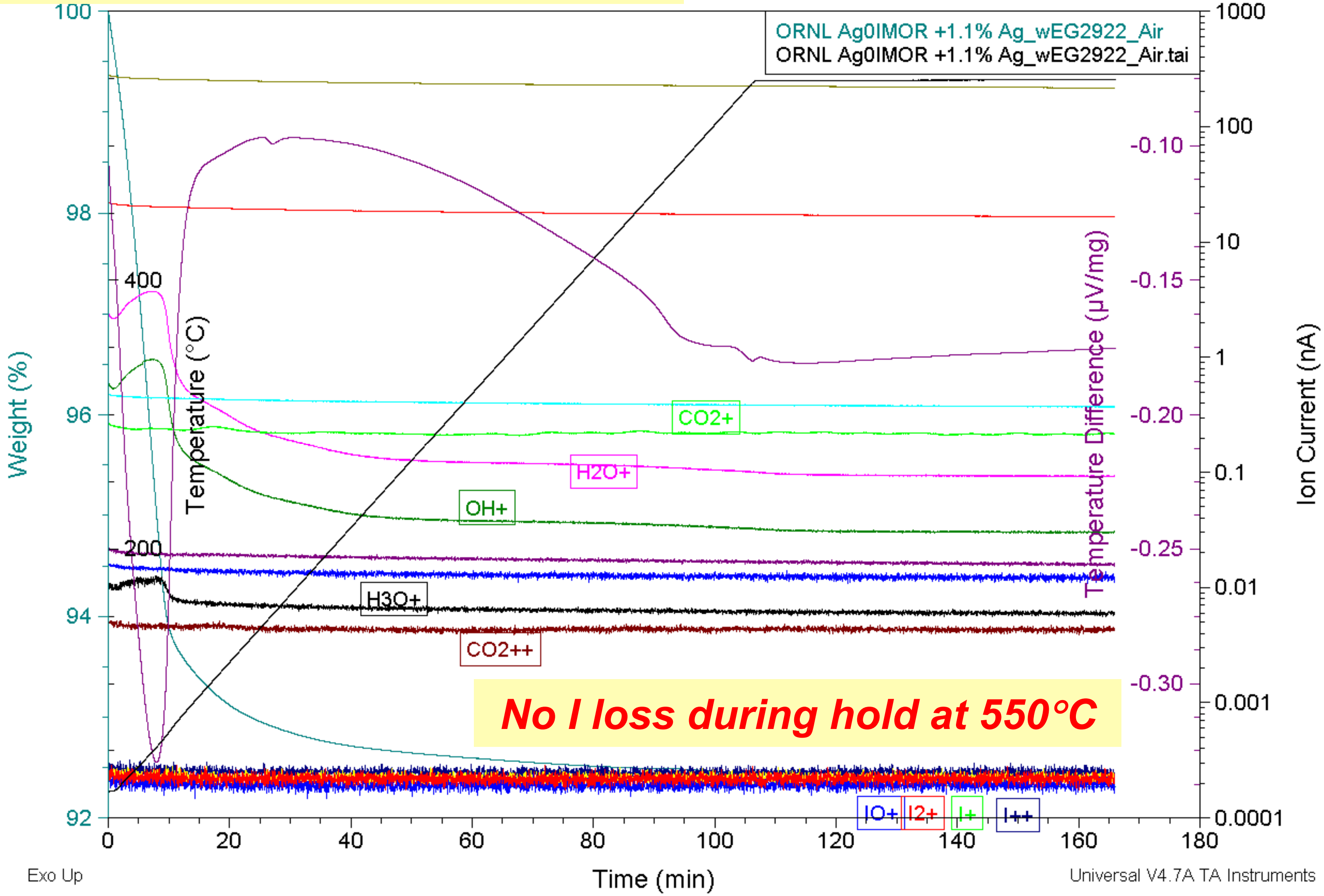
*For 20 wt% ORNL AgI-MOR + 80 wt% glass **+ 1.1 wt% Ag Flake***
5°C/min to 550°C for 1 hr



No I loss during hold at 550°C