SAND2015-7179R

Complete Initial Scoping Tests on the Incorporation of Novel Loaded Iodine Getters into GCM

Fuel Cycle Research & Development

Milestone M4FT-15SN0312044

DOE/NE-Fuel Cycle R&D
Materials Recovery and Waste Form Development

Prepared for
U.S. Department of Energy
Office of Nuclear Energy –
Separations Working Group
Tina M. Nenoff (Corresponding Author)
Terry J. Garino, Kenneth Croes
Sandia National Laboratories
August 18, 2015
FCRD-MRWFD-2015-000707

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U.S. DEPARTMENT OF ENERGY

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SUMMARY

This study encompasses initial scoping tests on the incorporation of a novel iodine loaded getter material into the Sandia developed low temperature sintering glass ceramic material (GCM) waste form. In particular, we studied the PNNL Ag-I-Aerogel. Optical microscopy indicates inhomogenous samples based on particle sizes and variations in color (AgI vs Ag/AgO on silica). TGA/MS data when heated in air indicates loss of iodine and organics (CO_2) between 250-450°C a total of ~15wt% loss, with additional / small iodine loss when during 550°C hold for 1 hr. TGA/MS data when heated in N_2 indicates less organic and slightly less iodine loss below 550°C, with no loss of iodine in 550°C 1 hour hold. Furthermore, a substantial mass loss of sulfur containing compounds is observed (m/e of 34 and 36) between 150 – 550°C in both air and N_2 sintering atmospheres. In an effort to capture iodine lost to volatilization during heating (at temps below glass sintering temperature of 550°C), we added 5 wt% Ag flake to the AgI-aerogel. Resulting data indicates the iodine is retained with the addition of the Ag flake, resulting in only a small iodine loss (< 1wt%) at ~350°C. No method of curtailing loss of sulfur containing compounds due to heating was successful in this scoping study.

ACKNOWLEDGEMENTS

The authors thank J. Metyas (PNNL) for AgI-aerogel samples. We acknowledge funding from the DOE/NE Fuel Cycle R&D – Materials Recovery and Waste Form Development (MRWFD). Sandia National Laboratories is a multi-program 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.

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1. ABBREVIATIONS AND ACRONYMS

Ag	Silver
Ag°	Silver metal
AgI	Silver Iodine
Bi	Bismuth
°C	Degrees Celsius
DSC	Differential Scanning Calorimetry
EDX	
FCRD	Fuel Cycle Research and Development
FY	Fiscal Year
g	Gram
GCM	Glass Composite Materials (waste form)
hr	Hour
I	Iodine
I_2	Iodine (gas)
INL	Idaho National Laboratory
L	Liter
min	Minute
MOR	Mordenite Zeolite
MS	Mass Spectroscopy
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
Si	Silicon
SNL	Sandia National Laboratories
SEM	Scanning Electron Microscopy
TGA	Thermo Gravimetric Analysis
XRD	X-ray Diffraction

2. INTRODUCTION

In the spent nuclear fuel reprocessing procedures under consideration by the US Department of Energy, off-gas containing $^{129}I_2$ and organic-^{129}I vapors is passed through a bed of a silver-exchanged Ag°-Mordenite (Ag°-MOR), that selectively captures the ^{129}I to form AgI–MOR.[1,2] The majority of the captured ^{129}I reacts with the silver in the Ag°-MOR to form AgI, while the rest is either chemically adsorbed, or passed downstream. Silver iodide (melting point = 558°C and density = 5.675 g/cm^3)[3] has a low solubility in water, 3 x 10^{-6} g/L at 20°C[3] (corresponding to a K_{sp} of $10^{-16.1}$), which makes silver a good candidate for the capture of ^{129}I. For safe storage, the AgI-MOR must be incorporated into a dense, durable solid waste form, so that the release of ^{129}I is inhibited with time or environmental contact. Because of their flexibility of synthesis and chemical durability, low temperature sintering glasses are being examined for the encapsulation of AgI-MOR iodine capture materials to form Glass Composite Materials (GCMs), for subsequent use as waste forms.[4-7] They are easier and less expensive to prepare than conventional ceramics but also offer high durability, as shown in our recent work.[8]

In our previous reports[5-8] on I_2-loaded Ag°-MOR, we identified a commercially available low-temperature sintering glass powder based on silicon and bismuth oxides that sinters to full density at 550°C and has excellent durability. To prevent surface/bulk chemisorbed I_2 vapor from escaping from the zeolite during GCM sintering, additional Ag flake was added to the GCM mixture to capture the desorbing I_2 vapor. As a note, little to no Ag flake is necessary if the GCM is sintered in inert atmosphere,[9] an option for future scaleup studies.

The purpose of the present scoping study is to study the scientific conditions of incorporating novel iodine getter materials (other than zeolite or metal-organic frameworks (MOFs)) into the GCM. Specifically, we focused the scoping study on the PNNL AgI-Aerogels,[10] the material characterization and needs for eventual incorporation into the GCM (eg., need for additional Ag flake to capture volatilized iodine during heating).

3. EXPERIMENTAL METHODS

3.1 Starting Materials

Approximately 6 grams of silver functionalized aerogel, partially loaded with iodine were provided to SNL from PNNL. Information provided indicated that the samples were from deep-bed methyl iodide adsorption testing at INL. Sample was fully characterized to better understand iodine fixation and release from the aerogel, in particular temperature and co-desorbed species that might affect GCM formation. To capture volatilized iodine during heating/sintering, various experiments utilized additional silver flake (<10 μm, Aldrich, Milwaukee, WI) mixed with the AgI-Aerogels.

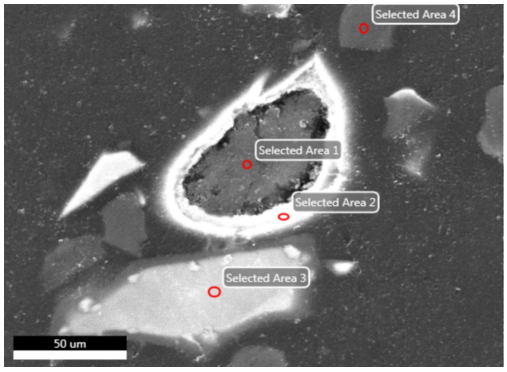
3.2 Characterization Methods

Simultaneous thermogravimetric analysis and differential scanning calorimetry (TGA/DSC, SDTQ600, TA Instruments, Newcastle, DE) with mass spectroscopic (MS, Thermo Star^{TM}, Pheiffer Vacuum, Inc., Asslar, Germany) off-gas analysis was performed on powder samples of the as-received AgI-aerogel materials, the powdered as-received aerogel materials, and the mixed AgI-aerogel with added Ag flake. Heating experiments were performed in both N_2 and in air at 5°C/min heating rate. Samples were also studied by powder X-ray diffraction (XRD, Siemens Kristalloflex D 500 diffractometer, Bruker-AXS Inc., Madison, WI) and scanning electron microscopy with energy dispersive spectroscopy (SEM, FEI NovaNano SEM 230 and EDS, EDAX Genesis Apex 2 with an Apollo SDD detector) to determine the elemental composition of the material. Optical microscopy was performed using an AM4013TL Dino-Lite Premier digital microscope.

3.3 AgI-Aerogel Characterization

The as-received AgI-aerogel was inhomogenous in appearance and in iodine loading as determined by dark color of AgI (see figure 1). Upon inspection by SEM-EDS, it is obvious that the AgI is a surface coating on individual particles (see figure 2). Upon heating to 550°C (the sintering temperature for the GCM), the majority of the AgI sinters as particles on the surface of each of the silica particles; strength of adhesion is not fully understood at this time (see figure 3).

Figure 1: Optical image of AgI-aerogel, as-received from PNNL.



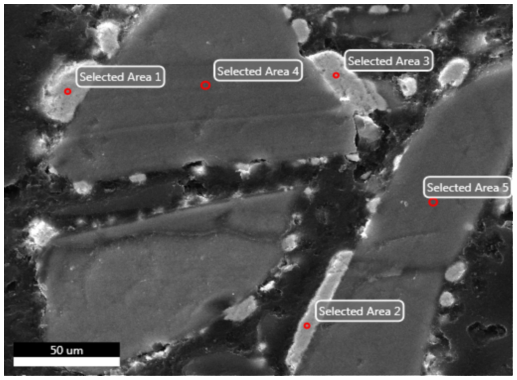
Area 1 EDS:

Element	Weight %	Atomic %	Net Int.	Error %
O K	38.31	53.31	762.86	9.21
SiK	50.38	39.93	9,082.71	3.43
S K	9.20	6.39	866.42	6.87
AgL	0.19	0.04	11.39	45.60
I L	1.93	0.34	100.46	12.60

Area 2 EDS:

Element	Weight %	Atomic %	Net Int.	Error %
O K	21.95	45.27	498.26	9.96
SiK	30.32	35.62	4,879.42	6.17
S K	7.70	7.92	1,079.68	6.64
AgL	17.02	5.21	1,514.48	2.92
I L	23.01	5.98	1,458.98	2.38

Figure 2: SEM-EDS of as-received AgI-aerogel; vast majority of AgI is on outer surface of particles.



Area 1 EDS:

Element	Weight %	Atomic %	Net Int.	Error %
O K	0.00	0.01	0.02	99.99
SiK	0.27	1.11	33.63	23.65
AgL	44.33	47.95	5,522.27	1.79
I L	55.40	50.93	3,784.39	3.62

Area 2 EDS:

Element	Weight %	Atomic %	Net Int.	Error %
O K	26.18	50.80	633.73	9.46
SiK	35.25	38.98	5,823.73	6.06
AgL	18.13	5.22	1,705.69	2.17
I L	20.44	5.00	1,331.00	2.36

Figure 3: SEM-EDS of post-sintered AgI-aerogel; AgI crystallized on outer surface of particles.

3.4 Thermal Characterization of AgI-Aerogel

TGA/MS: AgI-aerogel heated in air shows loss of I, CH_3I and I_2 from 250 – 450°C, see figure 4. However, heating in N_2 atmosphere results in minimum loss of iodine (see figure 5); presumably this is due to the fact that the organic functionalizing groups are not burning and releasing the AgI. However, there is enormous loss of sulfur containing compounds (eg., sulfur dioxide) as slow as 150°C in both the sintering in air and N_2. For full TGA/DSC/MS in air of as-received sample, see Appendix A.

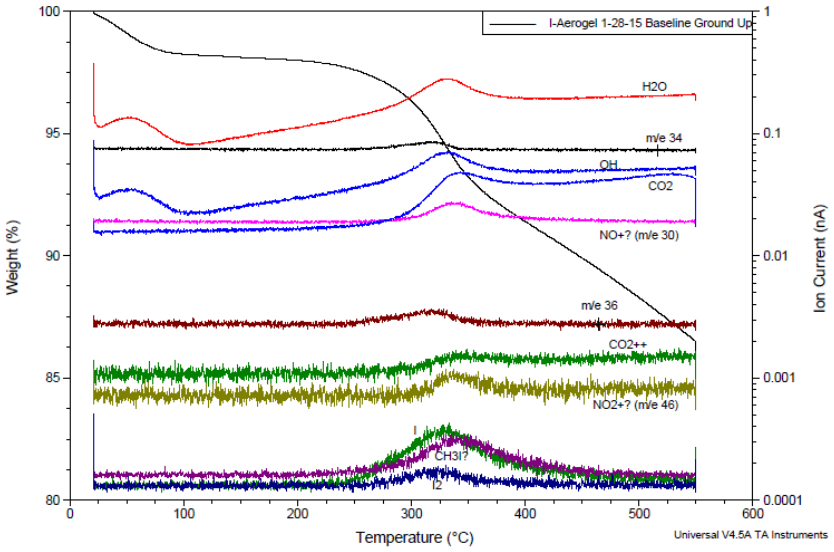


Figure 4: TGA/MS of AgI-aerogel heated in air; highlighted iodine species loss. Sulfur compound losses not shown here for clarity of iodine data.

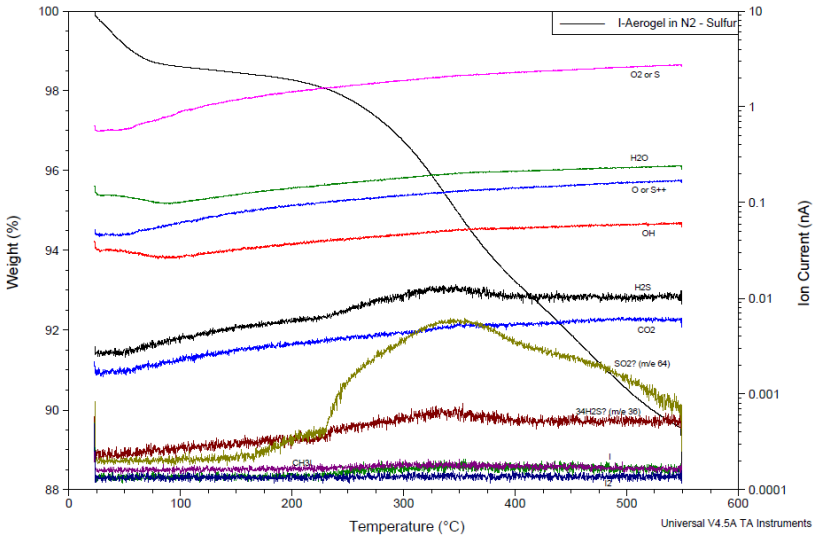


Figure 4: TGA/MS of AgI-aerogel heated in N_2; highlighted sulfur compound species loss.

4. Effect of addition of Ag flake to AgI-eerogel under Heat Treatment

TGA/MS: AgI-aerogel mixed with 5 wt% Ag flake results in minimal iodine loss at ~325°C. This indicates retention of the volatilized iodine by the formation of AgI in/on the aerogel. See figure 5.

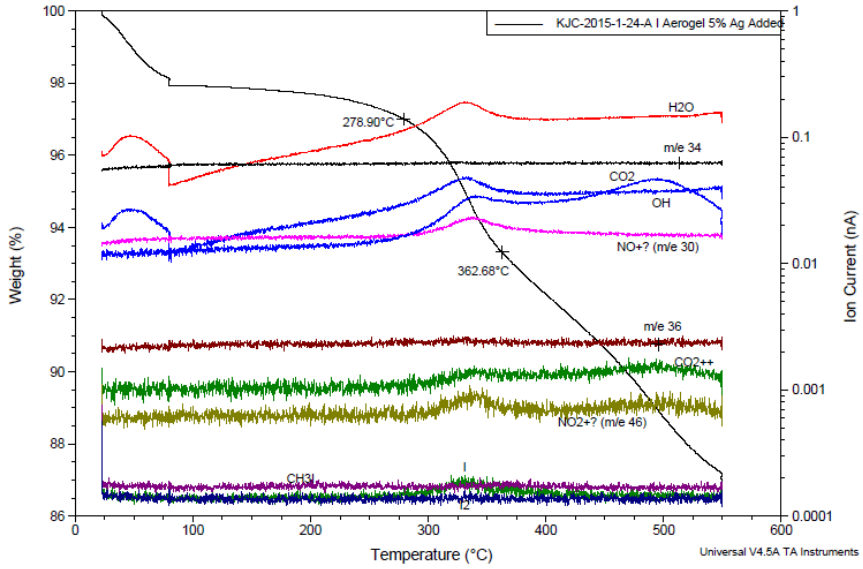


Figure 5: TGA/MS post Ag flake addition to AgI-aerogel; lack of iodine loss.

5. CONCLUSIONS

This study encompasses initial scoping tests on the incorporation of a novel iodine loaded getter material into the Sandia developed low temperature sintering glass ceramic material (GCM) waste form. In particular, we studied the PNNL Ag-I-Aerogel. Optical microscopy indicates inhomogenous samples based on particle sizes and variations in color (AgI vs Ag/AgO on silica). TGA/MS data when heated in air indicates loss of iodine and organics (CO_2) between 250-450°C a total of ~15wt% loss, with additional / small iodine loss when during 550°C hold for 1 hr. TGA/MS data when heated in N_2 indicates less organic and slightly less iodine loss below 550°C, with no loss of iodine in 550°C 1 hour hold. Furthermore, a substantial mass loss of sulfur containing compounds is observed (m/e of 34 and 36) between 150 – 550°C in both air and N_2 sintering atmospheres. In an effort to capture iodine lost to volatilization during heating (at temps below glass sintering temperature of 550°C), we added 5 wt% Ag flake to the AgI-aerogel. Resulting data indicates the iodine is retained with the addition of the Ag flake, resulting in only a small iodine loss (< 1wt%) at ~350°C. No method of curtailing loss of sulfur containing compounds due to heating was successful in this scoping study.

Limited sample supplies at PNNL resulted in only additional pure aerogel to SNL in FY15. With no additional material available, and under the written guidance of Sigma Team lead R. Jubin (July 7, 2015), no additional testing of the AgI-Aerogel (eg., incorporation into GCM or durability studies) were performed in this scoping study. We believe that future studies with additional material from PNNL, in which silver flake is added for volatilized iodine is captured to form AgI, the AgI-aerogels will be successfully incorporated into the GCM and retain the high durability performances recorded with AgI-MOR incorporation into the GCMs.[8]

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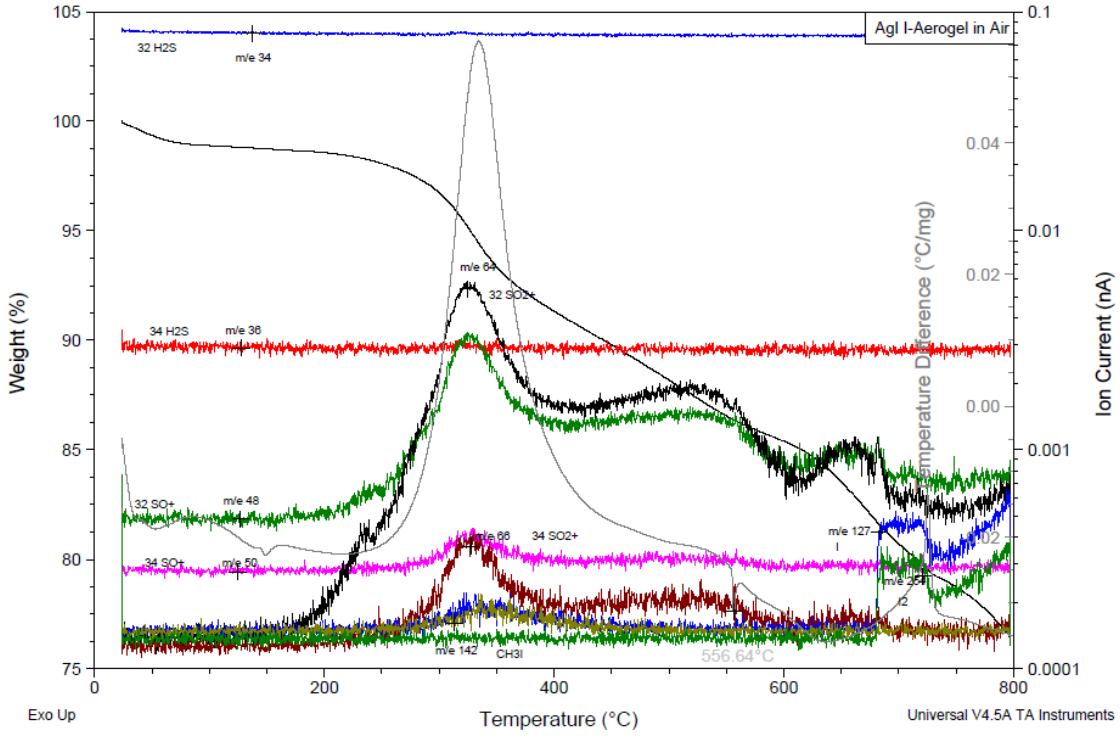
7. APPENDIX A

TGA/DSC/MS (25 - 800°C at 5°C/min), of AgI-Aerogel as received, sintered in air. Evidence of large sulfur compounds loss beginning at ~180°C, and iodine compounds' losses around 250°C; AgI melt (DSC) evidenced at 556°C.



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