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CH_3I Loading and Sintering Effects on AgI-MOR GCM Durability

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Tina M. Nenoff (Corresponding Author)
Patrick V. Brady
Curtis D. Mowry
Terry J. Garino
Sandia National Laboratories

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Tina M. Nenoff, Patrick V. Brady, Curtis D. Mowry, and
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SUMMARY

Herein, we study the durability of the Sandia low temperature sintering Bi-Si oxide Glass Composite Material (GCM) waste form when formulated with Ag-MOR that has been exposed to a complex off gas stream that contains gaseous water, CH_3-I, NO and NO_2. The post-exposure MOR material was provided to SNL by INL.

Previously, the sintering history of I_2-loaded Ag-Mordenite encapsulated in a low temperature Bi-Si Glass Composite Material (GCM) showed no impact on release rates of Ag and I at 25 ^{o}C and pH ~ 5 - 6. Iodine and Ag release is controlled by the low solubility of an amorphous, hydrated silver iodide, not by the surface-controlled dissolution of I_2-loaded Ag-Mordenite. Furthermore, earlier studies at SNL indicate that the Ag-MOR exposed to this complex stream resulted in AgI-MOR with trace organic and iodine species; durability results for the GCM fabricated with this AgI-MOR (either as-made or post 550°C heat treatment) indicate releases of Ag and I at the same low rates as I_2-loaded AgI-MOR GCM, and by the same mechanism.

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CONTENTS

TABLES

FIGURES

ABBREVIATIONS AND ACRONYMS

AgI	Silver Iodine
Al	Aluminum
ASTM	American Society for Testing and Materials
Bi	Bismuth
°C	Degrees Celsius
CH_3I	Methyl iodide
cm	Centimeter
d	diameter
FCRD	Fuel Cycle Research and Development
GCM	Glass Composite Materials (waste form)
I_2	Iodine (gas)
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
INL	Idaho National Laboratory
μ	Micro
M	mole/liter
MOR	Mordenite Zeolite
O	Oxygen
s	Second (time)
Si	Silicon
SNL	Sandia National Laboratories
SPFT	Single Pass Flow Through test
XRD	X-ray Diffraction
Zn	Zinc

1. INTRODUCTION

The chemical and physical controls over iodine release from candidate ^{129}I waste forms must be quantified to predict long-term waste form effectiveness. Ag-Mordenite will likely be an important waste form component because of its ability to remove ^{129}I from waste streams and convert it to AgI and/or sorb it (e.g. Chapman et al., 2010). Silver iodide is relatively insoluble in water, $K_{sp} = 10^{-16.1}$ at 20°C, so Ag-Mordenite should retain ^{129}I for long periods of time. Encapsulating ^{129}I-loaded Ag–Mordenite (AgI–MOR) into a durable solid waste form should limit potential releases of ^{129}I further. Low temperature sintering Glass Composite Materials (GCMs) are candidates for encapsulating AgI-MOR. GCMs contain both crystalline and glass phases, and are easier to synthesize, less expensive, and can achieve higher waste loadings than traditional ceramic waste forms (e.g. Garino et al., 2011).

Herein we study the durability of the Sandia low temperature sintering Bi-Si oxide Glass Composite Material (GCM) waste form when formulated with Ag-MOR that has been exposed to a complex off gas stream that contains gaseous water, CH_3-I, NO and NO_2; material provided to SNL by INL (Soelberg 2014). This combined deep bed sorption testing, materials characterization and crystallographic study (including a differential Pair Distribution Function (d-PDF) analysis of the guest molecules in the MOR), indicated that the Ag-MOR exposed to this complex stream resulted in AgI-MOR with trace organic and iodine species on the bulk surface of the MOR (Nenoff et al., 2014).

To understand the durability of this new AgI-MOR, we use a Single Pass Flow Through (SPFT) test to determine if the sintering history affects the rate at which iodine and silver are released from the GCM AgI-MOR waste form. We study the effects of thermal pretreatment of the AgI-MOR (with trace contaminants) on the durability. We also measure the effect of loading by CH_3I, versus I_2, on GCM AgI-MOR durability. These results complement our previous efforts to document iodine loading, pH, temperature, and particle size impacts on the durability of the GCM AgI-MOR waste form (Nenoff et al., 2012, 2013a, 2013b, 2014).

2. EXPERIMENTAL METHODS

AgI-Mordenite and GCM Preparation

Two CH_3I-loaded samples were prepared using 20 wt% CH_3I-loaded AgI-MOR from INL (test #4, 9/20/2013, bed 2, ~5.2 wt% I_2), 80 wt% Ferro EG2922 glass powder, and an additional 1.1 wt% of Aldrich silver flake. Ferro EG2922 glass powder is a commercially available Bi–Si-oxide glass (3 μm average particle size, a density of 5.8 g/cm^3, coefficient of thermal expansion of 7.8×10^{-6} / °C, from Ferro Corp., Cleveland, OH). The glass has a composition of: 7.8 wt% ZnO, 63.4 wt% Bi_2O_3, 5.4 wt% Al_2O_3, 23.4 wt% SiO_2. An amount of Aldrich silver flake equal to 5.5 % of the mass of the AgI-MOR was also added to react with the I_2 vapor that desorbs from the AgI-MOR during heating.

For one of these samples, ***Sample 1 - INL CH_3I*** (Post preparation heat treatment to drive off bulk surface contaminants prior to incorporation into GCM): 600°C, 550°C 30 min, the AgI-MOR was preheated to 600°C at 5°C/min to remove organic components. The other sample, ***Sample 2 - INL CH_3I*** (As received): 550ºC 30 min, was not preheated. In both studies, the AgI-MOR was crushed with an alumina mortar and pestle and passed through a 150 μm sieve and then the AgI-MOR, glass, and Ag were wet mixed, dried and pressed into pellets at 5,000 psi. They were then densified by heating in air at 5°C/min to 550°C and holding at 550°C for 30 minutes.

After sintering, the samples were hand ground with an alumina mortar and pestle to < 38 μm before spex milling (8000M, Spex Sample®Prep®, Metuchen, NJ) for 10 minutes using an silicon nitride mill and ball. The surface area was measured using the BET method. The ground materials had BET surface areas of 4.8731 (*Sample 1 INL CH_3I* 600°C, 550°C 30 min) and 4.1837 (*Sample 2 INL CH_3I* As received, 550ºC 30 min).

Single-Pass Flow-Through Test

The Single Pass Flow Through Test Method (ASTM C-1662) is traditionally used to measure nuclear waste glass dissolution rates in aqueous solutions at T < 100°C. Waste form component release rates are measured by exposing a high surface area waste form sample in a reactor to a continual flow of solution and measuring waste form component concentrations in the effluent (e.g. Chou and Wollast, 1985). 4 reactors were constructed of Tygon tubing and pipette tips containing 0.2 g of each AgI-MOR waste form. The input solution, 0.01M NaCl was pumped through the reactor beds at a rate of 0.18 L/day. Dissolution measurements were made at 25°C.

Effluents were analyzed for pH, and for Ag, I, Zn, and Si, effluent levels in ppb, by ICP-MS in semi-quantitative mode (Table 1). Samples were tested for pH immediately following ICP-MS analysis using an Orion (Thermo Fisher Scientific, Waltham, MA) model 720A pH meter. The pH probe was calibrated using a 3-point calibration at 25°C (pH: 4.00, 7.00 and 10.00) using buffered pH standards (Thermo Fisher Scientific, Waltham, MA). Each water sample was measured in triplicate. The pH probe was rinsed with DI water after every reading, and the excess rinse water gently blotted off the probe to prevent any carryover to the sample tubes. After every 6 individual readings the pH probe was rechecked with a pH = 7.0 calibration solution to verify that drift was not occurring. Tabulated pHs represent the average of 3 measurements.

Table 1. SPFT effluent levels (ppb) and AgI concentration product.

Sample	Hours	pH	Si	Ag	I	Zn	log[Ag][I]
Sample 1 - INL CH_3I 600°C 550°C 30 min							
1	50	6.98	267	31.6	9.4	333	-13.67
2	54	6.51	265	30.4	17.0	345	-13.43
3	76	6.57	293	27.3	18.2	294	-13.44
4	97	6.11	313	26.4	13.6	258	-13.59
5	99	6.48	296	28.3	13.6	281	-13.56
6	100	6.40	298	27.9	9.6	272	-13.71
7	123	6.12	321	27.3	10.8	240	-13.67
Sample 2 - INL CH_3I As received 550ºC 30 min							
1	50	6.21	242	29.2	10.6	287	-13.65
2	54	5.56	243	27.7	20.4	335	-13.39
3	76	5.37	302	25.6	22.7	258	-13.38
4	97	5.66	339	25.0	13.5	233	-13.61
5	99	6.18	338	25.6	11.7	240	-13.66
6	100	5.88	347	25.1	11.0	235	-13.70
7	123	5.64	343	26.1	11.4	215	-13.67

3. RESULTS

Steady-state effluent pHs were ~ 5.8 – 6.1 for each run. Ag effluent levels reached steady-state values within ~ 2 days and are essentially the same for each waste form, in the range of 26 - 27 ppb (Figure 1). Steady state iodine effluent levels were ~ 11 ppb and reached constant, steady-state values after ~ 4 days of reaction (Figure 1). There is little or no effect of CH_3I-

loading, or sintering history, on effluent silver iodine levels. The relative constancy of Ag and I levels supports the hypothesis that AgI solubility controls Ag and I release. Note that the log product of the measured Ag and I levels cluster around a constant value of $10^{-13.7}$, which is higher than the theoretical AgI solubility product of $10^{-16.1}$. Ag and I are most likely being released from a more soluble, amorphous and possibly hydrated, AgI phase in the dissolving waste form.

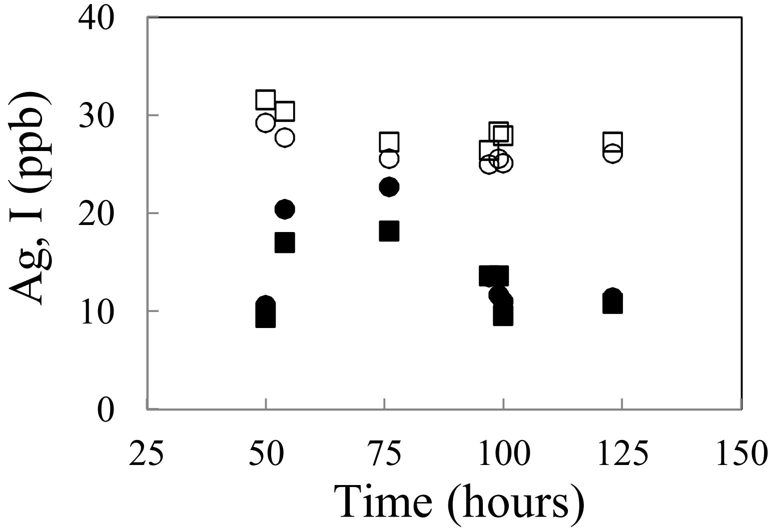

Figure 1. Ag (unfilled symbols) and I (filled symbols) effluent levels as a function of time. Circles = Sample 1 (post heat treatment); squares = Sample 2 (as-made, no heat treatment).

4. CONCLUSIONS AND FUTURE WORK PLANS

As part of our ongoing research effort to understand the durability and material processability of the low temperature sintering Sandia Waste Form for iodine capture materials, we have undertaken a study in which the effect of sintering and CH$_3$I loading have on the durability of the AgI-MOR GCM . Sintering and CH$_3$I loading AgI-MOR in a GCM waste form have little effect on iodine or silver release because, as expected, both are limited by the low solubility of AgI. The higher effluent portion of Ag relative to I (Figure 1) suggests that Ag leaching from the waste form controls equilibrium levels of iodine. Higher Ag leach rates will lower I levels issuing from a degrading waste form. Ongoing research in FY14 includes the determination of the maximum loading level of AgI-MOR (from I$_2$ gas stream) on the durability of this GCM waste form.

5. REFERENCES

ASTM “Standard Practice for Measurement of the Glass Dissolution Rate Using the Single-Pass Flow-Through Test Method” Accessed 11/08/2012.

Chapman, K; Chupas, P.; Nenoff, T.M. “Radioactive Iodine Capture in Silver-Loaded Zeolites Through Nanoscale Silver Iodide Formation” *J. Amer. Chem. Soc.*, **2010**, *132*(26), 8897–8899.

Chou, L.; Wollast, R. “Steady-State Kinetics and Dissolution Mechanisms of Albite” *Am. J. Science*, **1985**, *285*, 963-993.

Garino, T.J.; Nenoff, T.M.; Krumhansl, J.L.; Rademacher, D. “Low-Temperature Sintering Bi-Si-Zn Oxide Glasses For Use in Either Glass Composite Materials or Core/Shell ^{129}I Waste Forms”, *J. Amer. Ceram. Soc.* **2011**, *94*(8), 2412-2419; and references within.

Nenoff, T.M.; Brady, P.V.; Garino, T.J.; Mowry, C.D. “Determination of Baseline Iodine Waste Form Performance Characteristics”, FCRD-SWF-2012-000172, SAND 2012-6892C, 2012.

Nenoff, T.M.; Brady, P.V.; Mowry, C.D. “Effect of pH and Temperature on AgI-Mordenite and Bi-Si Glass Dissolution” FCRD-SWF- 2013-000098, SAND 2013-1205P, 2013a.

Nenoff, T.M.; Brady, P.V.; Garino, T.J.; Mowry, C.D. “SPFT Testing of Optimized Weight Loadings of AgI-Z in GCM”, FCRD-SWF-2013-000215, SAND 2013-5763P, 2013b.

Nenoff, T.M.; Brady, P.V.; Garino, T.J.; Mowry, C.D. “Effect of Particle Size on Iodine Loaded Ag-MOR on Final GCM Waste Form”, FCRD-SWF-2014-000472, SAND 2014-4846P, 2014.

Nenoff, T.M. Nenoff, T.M.; Rodriguez, M. A.; Soelberg, N.; Chapman, K. A. “Silver-Mordenite for Radiological Gas Capture from Complex Streams: Dual Catalytic CH_3I Decomposition and I Confinement”, *Micro. Meso. Mater.,* **2014**, in press (Invited, *special issue cluster for Thomas Bein*), DOI: 10.1016/j.micromeso.2014.04.041

Soelberg, N. “Chemisorption of Methyl Iodide”, INL/MIS-14-32211, FCRD- FCRD-SWS-2014-000457, May 2014.

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Global Nuclear Energy Partnership (NE-2.4)
U.S. Department of Energy
1000 Independence Ave. SW
Washington, DC, 20585

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