

Optimization studies on GCM for iodine waste forms

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We are pursuing an understanding of the durability and materials processability of the low temperature sintering Bi-Si oxide Glass Composite Material (GCM)¹ Waste Form for iodine capture materials. The chemical and physical controls over iodine release from candidate ¹²⁹I 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 ¹²⁹I from waste streams and convert it to AgI and/or sorb it. Silver iodide is relatively insoluble in water, $K_{sp} = 10^{-16.1}$ at 20°C, so Ag-Mordenite should retain ¹²⁹I for long periods of time. Encapsulating ¹²⁹I -loaded Ag-Mordenite (AgI-MOR) into a durable solid waste form should limit potential releases of ¹²⁹I further.

In FY14 we studied the effects of a number of synthesis variables to assess their effects on the durability of the Sandia GCM waste form. Those variables included: **AgI-MOR weight percent level, AgI-MOR particle size, organic iodine source, silver addition, and sintering atmosphere**. We use a Single Pass Flow Through (SPFT)² test to determine variables that might affect the rate at which iodine and silver are released from the waste form, and therefore its durability. These results complement our ongoing GCM waste forms studies for iodine.³⁻⁹

AgI-MOR weight percent levels: GCM fabricated with 22 and 25% AgI-MOR SPFT testing indicates releases of Ag and I at the same low rates as 15% AgI-MOR GCM, and by the same mechanism. Iodine and Ag release is controlled by the low solubility of an amorphous, hydrated silver iodide, not by the surface-controlled dissolution of I₂-loaded Ag-Mordenite. Based on this data, we postulate that much higher loading levels of AgI-MOR are probable in this GCM waste form, and limits will govern by retention of mechanical integrity of the GCM versus the solubility of silver iodide.

AgI-MOR particle size: The samples studied included 3 different particle sizes of AgI-MOR encapsulated in the Bi-Si Glass to form GCM waste forms: **< 350 μm, < 150 μm, and < 75 μm**. These sizes were chosen as they bracket and/or duplicate the original sizes studied of < 150μm and < 45μm. This study shows that the AgI-MOR particle size in a GCM waste form has no 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 suggests that Ag leaching from the waste form controls equilibrium levels of iodine.

Organic iodine source: The GCM waste form was formulated with Ag-MOR that has been exposed to a complex off gas stream that contains gaseous water, CH₃-I, NO and NO₂. Iodine and Ag release is controlled by the low solubility of an amorphous, hydrated silver iodide, not by the surface-controlled dissolution of I₂-loaded Ag-Mordenite. Earlier studies at SNL in which 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 I₂-loaded AgI-MOR GCM, and by the same mechanism.

Silver Addition, Sintering Atmosphere: The minimum amount of silver flake required to prevent loss of I₂ during sintering in air for a SNL GCM Waste Form containing AgI-MOR (ORNL, 8.7 wt%) was determined to be 1.1 wt% Ag. The final GCM composition prior to sintering was 20 wt% AgI-MOR, 1.1 wt% Ag, and 80 wt%

Bi-Si oxide glass. Alternatively, heating the AgI-MOR in inert atmosphere instead of air allowed for densified GCM formation without I_2 loss, and no necessity for the addition of Ag. The cause of this behavior is found to be related to the oxidation of the metallic Ag to Ag^+ when heated to above $\sim 300^\circ C$ in air. Heating rate, iodine loading levels and atmosphere are the important variables that determine AgI migration and results suggest that AgI may be completely incorporated into the mordenite structure by the $550^\circ C$ sintering temperature.

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Nenoff, et. al., DOE/NE-SWG related publications in FY14:

1. Terry J. Garino, **Tina M. Nenoff**, Mark A. Rodriguez; FCRD-SWF-2014-000286, Milestone M3FT-14SN0312042, DOE/NE-Fuel Cycle R&D Separations Working Group, “Determine Minimum Silver Flake Addition to GCM for Iodine Loaded AgZ”, Sandia National Laboratories April 1, 2014
2. **Tina M. Nenoff**, Patrick V. Brady, Curtis D. Mowry, Terry J. Garino, FCRD-SWF-2014-000591, DOE/NE-Fuel Cycle R&D Separations Working Group, M4FT-14SN0312045, “CH₃I Loading and Sintering Effects on AgI-MOR GCM Durability”, Sandia National Laboratories, August 16, 2014,
3. **Tina M. Nenoff**, Mark A. Rodriguez, Sandia National Laboratories, Nick R. Soelberg, Idaho National Laboratory, Karena W. Chapman, Advanced Photon Source, Argonne National Laboratory, FCRD-SWF-2014-000471, DOE/NE-Fuel Cycle R&D Separations Working Group, M4FT-14SN0312041, “Determine Mechanism of CH₃I Capture in AgZ”, August 16, 2014,
4. **Tina M. Nenoff**, Patrick V. Brady, Curtis D. Mowry, Terry J. Garino, FCRD-SWF-2014-000472, DOE/NE-Fuel Cycle R&D Separations Working Group, Milestone M4FT-14SN0312044, “Effect of Particle Size on Iodine Laded Ag-MOR on Final GCM Waste Form”, Sandia National Laboratories, June 16, 2014,
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Nenoff, et. al., DOE/NE-SWG related Patents Awarded and Filed in FY14:

1. Provisional Patent filed, **Tina M. Nenoff**, Dorina F. Sava Gallis, Karena W. Chapman, Peter J. Chupas “*System and method for the capture and storage of waste*”; 10/23/2013.
2. Provisional Patent filed, **Tina M. Nenoff**, Dorina F. Sava Gallis, Terry J. Garino, “*Densified waste form and method for forming*”; 11/15/2013