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OPTIMIZATION OF SINTERED AgI-MORDENITE COMPOSITES FOR ^{129}I STORAGE

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The thermal processing of a proposed durable waste form for ^{129}I was investigated. The waste form is a composite with a matrix of low-temperature sintering glass that encapsulates particles of AgI-mordenite. Ag-mordenite, an ion-exchanged zeolite, is being considered as a capture medium for gaseous $^{129}I_2$ as part of a spent nuclear fuel reprocessing scheme under development by the US DOE/Nuclear Energy (NE). The thermal processing of the waste form is necessary to densify the glass matrix by viscous sintering so that the final waste form does not have any open porosity. Other processes that can also occur during the thermal treatment include desorption of chemisorbed I_2, volatilization of AgI and crystallization of the glass matrix. We have optimized the thermal processing to achieve the desired high density with higher AgI-mordenite loading levels and with minimal loss of iodine. Using these conditions, 625°C for 20 minutes, the matrix crystallizes to form a eulytite phase. Results of durability tests indicate that the matrix crystallization does not significantly decrease the durability in aqueous environments.

I. INTRODUCTION

^{129}I is a component of spent nuclear fuel[1] with a long half-life (>1.6 x 10^7 yrs) and the potential to be mobile in the environment.[2] When spent fuel is reprocessed, the ^{129}I can be isolated from the other radioactive components and then incorporated into a durable waste form designed especially for it to restrict its release into the environment over time. In the spent nuclear fuel reprocessing process under development by the US DOE/NE, $^{129}I_2$ vapor is passed over Ag-exchanged mordenite, a zeolite, to form silver iodide (AgI).[3] Silver iodide has low aqueous solubility compared to other iodides, 1.3 x 10^{-7} *M* at 20°C.[4] However, it also has a relatively low melting point (558°C) and an appreciable vapor pressure at higher temperatures,[4] which limits the temperature at which a waste form can be processed. We have developed a waste form containing AgI-mordenite (AgI-MOR) that utilizes a low temperature sintering oxide glass that encapsulates the AgI-MOR particles to form a dense and durable glass composite material (GCM).[5,6] Sintering as opposed to melting allows a more durable glass composition to be used since glasses that melt in this temperature range are typically not very durable. We have utilized a bismuth silicate based glass that can be sintered to full density at 550°C and yet has excellent chemical durability. To fabricate the composite waste form, the glass powder is mixed with ground AgI-MOR, pressed into a compact pellet and then sintered to form a dense and durable waste form.

In the earlier work,[5,6] we fabricated mock waste forms using 20 wt% AgI-MOR that was ground to <150 µm before mixing with the glass and an additional 5 wt% of silver flake. After pressing, the heat treatment was to 550°C for 1hr. This resulted in a dense waste form with an amorphous glass phase matrix surrounding the AgI-MOR and AgI particles. Durability studies on this material indicated comparability with other glass based waste forms.[6,7]

The work reported herein was undertaken to explore how processing and compositional variables that differ from the baseline effect the waste form and its durability in order to optimize its performance. The results of experiments designed to maximize the loading of AgI-MOR in the composite while maintaining high density and limiting any loss of iodine during processing will be described. Iodine loss can occur from desorption of chemisorbed iodine from the MOR above 250°C and from the AgI above 550°C. Thermogravimetric analysis (TGA) combined with mass spectrometry off-gas characterization were used to determine both the amount of silver powder that needs to be added to react *in situ* with the desorbing I_2 and the rate of AgI volatilization as a function of processing temperature. The effects of AgI-MOR particle size, loading level and the heat treatment temperature were studied. Higher processing temperatures were then shown to allow an increased amount of AgI-MOR to be incorporated while still achieving a non-porous structure. However, the higher temperature led to the crystallization of the glass. The effect of the presence of the crystalline phase, eulytite, on the durability was determined using Product Consistency Testing[8] (PCT), and MCC-1[9] Testing on sintered waste forms. The results of these studies indicate that a higher amount of AgI-MOR can be incorporated by increasing the heat treatment temperature without compromising durability.

II. EXPERIMENTAL PROCEDURE

The glass powder used was EG2922 (ρ = 5.8 g/cm^3, Ferro Corp., Cleveland, OH) and has a composition determined by EDS of 44 mol % SiO_2, 32 mol % Bi_2O_3, 20 mol % ZnO and 5 mol % Al_2O_3 and can be sintered to full density at 550°C in 1 hr without crystallization. A synthetic MOR (LZM5, Ionex Research Corp., Lafayette, CO) used was ion exchanged using a 0.1 M silver nitrate solution at 90C for several hours and then dried. The Ag+-MOR was then reduced to Ag°-MOR by heating in 3% H_2 to 500°C for 1 hr. The Ag°-MOR was then exposed to I_2 vapor at 90°C for 24 hr followed by 24 hr at 90C in an open container to remove any excess iodine. The resulting fully loaded AgI-MOR contained ~22 wt% iodine. Lower iodine loading levels will most likely be the case in an implemented reprocessing program.

The AgI-MOR was then crushed using an alumina mortar and pestle and sieved to several size fractions such as <150 µm and <45 µm. Prototype composite waste form samples were made by mixing the appropriate amounts of glass powder and crushed AgI-MOR with an aqueous binder solution containing polyvinyl alcohol and polyethyleneglycol binders, drying and then cold uniaxial pressing in a steel die set (1.27 cm diam). The AgI-MOR content was varied from 15 to 25 wt%. Silver flake (Sigma Aldrich, St. Louis, MO) was added unless otherwise mentioned to react with any I_2 vapor and that desorbs during heat treatment. A series of samples with 20 wt% AgI-MOR were prepared that had different Ag flake addition levels of 0, 2, 3, 4 or 5 wt%. These samples were used to determine the amount of silver required to react with all the desorbed I_2. This was done by heating some of the pressed mixture in a TGA (TA Instruments, New Castle, DE) with simultaneous mass spectrometryanalysis (Thermo Star^{TM}, Pfeiffer Vacuum GmbH, Asslar, Germany) of the off-gas.

The volatility of AgI from the waste form prototypes was also studied using the same thermal analysis equipment. Pressed mixtures with 20 wt% AgI-MOR and 5% added Ag flake were heated at 10°C/min to either 550°C or 650°C. The vapor pressure of AgI varies from ~0.007 to ~0.06 torr over this temperature range.[4]

Pellets with various AgI-MOR loadings were sintered in air on boron nitride coated alumina plates to temperatures from 550° to 650°C with a 5°C/min heating rate and hold times up to 1 hr. The effect of the MOR particle size was also studied using pellets with 20 wt% of AgI-MOR that were ground and sieved to various size fractions (<150 µm, <106 µm, <45 µm, <20 µm and < 10 µm). The sintering shrinkage during the heat treatment was also measured using a video imaging system that allowed taking digital images of a small piece of a 20 wt% AgI-MOR sample.

Sintered samples were characterized using X-ray diffraction (XRD, D500, Siemens Rontgenwerk, Rudolstadt, Germany) and scanning electron microscopy (NovaNano SEM 230, FEI, Hillsboro, OR). *In situ* XRD patterns were also taken during the heat treatment of 20 wt% AgI-MOR samples from room temperature to 550°C.

Samples were prepared for PCT and MCC-1 testing using a composition of 15 wt% AgI-MOR. Two sets were prepared: one with amorphous glass phase that were sintered at 550°C for 20 min and the other with crystallized glass phase that were sintered at 575°C for 1 hr. The samples were analyzed by XRD to verify whether or not the eulytite was present and then ground and sieved appropriately for the PCT and for the MCC-1; the surfaces were ground to a 600 grit finish using SiC paper. After one week of treatment at 90°C in de-ionized water inside polytetrafluoroethylene containers, the leachates from the PCT tests were analyzed using ICP-MS (Elan 6100 DRC, Perkin Elmer, Groton, CT). Liquids were aspirated directly into the instrument without modification and the instrument was operated in the semi-quantitative mode. This mode compares signal from a multi-element standard analyzed the same day with known relative instrument response factors to calculate concentration of those elements detected in the sample. Two multi-element standards (CLMS-1 and CLMS-2, Spex Certiprep, Metuchen, NJ), covering 46 elements, were used for these tests. The surfaces of the MCC1 pellets were examined in the SEM. Energy dispersive spectroscopy (EDS, EDAX Genesis Apex 2 with an Apollo SDD detector) was used to determine the elemental composition of the crystalline material on the surface of the pellets.

III. RESULTS AND DISCUSSION

III.A. Additional Silver Addition Determination

Fig. 1 shows the TGA and off-gas analysis for a sample of mixed glass and 20 wt % of -45µm AgI-MOR that did not contain any added silver. Iodine begins to leave the sample at 250°C and continues to leave all the way to the maximum temperature of 550°C as evidenced by the increased slope of the mass loss and the presence of I detected by the MS. When silver was added, the onset of the slope changed and I detection shifted to increasingly higher temperatures, while the amount of mass loss decreased accordingly. With 2% added Ag, the iodine started to leave at 300°C and the total mass loss was 1.5% lower. Thus, the desorbing iodine reacts with the added silver to form AgI until the silver is essentially depleted.

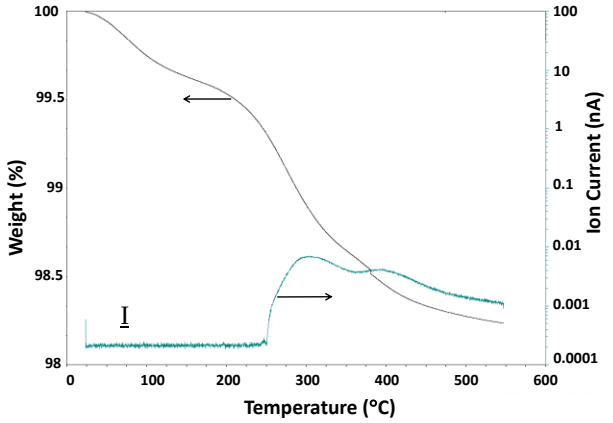

Fig. 1. Mass loss and Iodine off-gas MS analysis for a sample with no added Ag.

Fig. 2 shows the data with 4% added silver. At this level, only a small amount of iodine is lost starting above 500°C. Plotting the additional mass lost above that lost for a sample with 5% silver and no iodine loss (all samples lose a small amount of mass from water) as a function of added amount of silver indicates that 4.1% of silver is needed for this level of fully loaded AgI-MOR to fully react with the adsorbed iodine, or a ratio of Ag to AgI-MOR of 0.205.

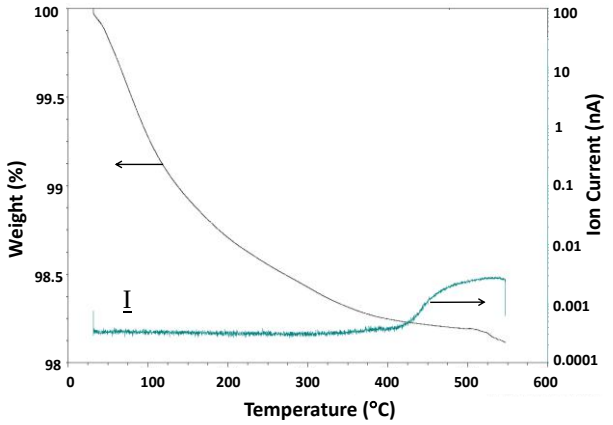

Fig. 2. Mass loss and Iodine off-gas MS analysis for a sample with 4 wt% Ag added.

III.B. Silver Iodide Volatility During Sintering

During the heat treatment of the composite waste forms, AgI can sublimate or evaporate from the surface of the waste form due to its appreciable vapor pressure in the temperature range needed to reach high density. The TGA and off-gas analysis of a sample of 20 wt% AgI-MOR with 5% added Ag flake is shown in Fig. 3. The sample was heated to 550°C and then held isothermally for 1 hr followed by heating to 650°C for and holding for 1hr. At

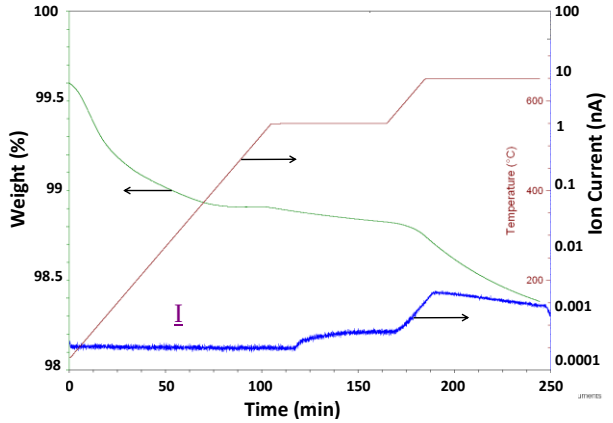

Fig. 3. The TGA/Iodine off-gas analysis for a 20 wt% AgI-MOR pressed sample with 5% Ag during heating to and holding at 550°C for 1 hr and then to 650°C for 1 hr.

both temperatures, iodine is detected in the off-gas. The rate of mass loss is significantly higher at 650°C than at 550°C, as expected. No silver was detected in the off-gas since it is expected to plate out in the transfer line to the MS.

The rate of mass loss decreases with time at 650°C because the surface region becomes depleted of AgI. If the initial slope at 650°C is used to compute the rate of iodine loss, the rate is nearly 5 times higher at 650°C than at 550°C. Since AgI is 54 wt% iodine and taking into consideration the initial mass and the dimensions of the sample (0.1 cm^2 surface area), the specific rates of iodine loss are 4.9 x 10^{-4} g I/cm^2/hr and 2.4 x 10^{-3} g I/cm^2/hr at 550° and 650°C, respectively. Even though the rate is significantly higher at 650°C as expected due to the higher AgI vapor pressure, the total fraction of iodine lost could still be quite small for larger samples with smaller surface area to volume ratios, especially if complete densification can be achieved in a relatively short time at temperature. For example, for a cylindrical sample with 20 wt% fully loaded AgI-MOR with diameter and thickness of 5 cm, only 0.56% of the iodine would escape after 20 min at 650°C.

III.C. Composite Densification During Sintering

In situ sintering experiments using the imaging system to measure shrinkage during the composite densification showed that most of the shrinkage occurs during the heating and the first 20 min of the hold at the maximum temperature for temperatures from 550° to 650°C. A series of 1.27 cm diameter pressed pellets with 25 wt% AgI-MOR were heated to various temperatures in this range for 20 min with a 5°C/min heating rate. After wards, they were soaked in water to determine the relative level of open porosity. As shown in Fig. 4, the sample heated to 625°C was non-porous with essentially no gain

in mass after soaking in water. Lower loading levels could be sintered to high density at lower temperatures.

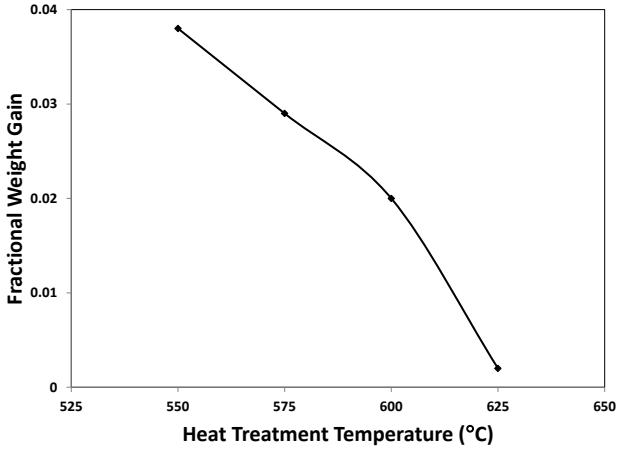

Fig. 4. Fractional increase in mass of samples heat treated for 20 min at different temperatures after soaking in H_2O.

III.D. Glass Crystallization and Microstructure

XRD analysis of the base glass and of a mixture of 15 wt% Ag-MOR (not loaded with iodine) and 85 wt% of the glass after heating for 1 hr at 550°C shows that no crystallization of the glass occurs. However, when samples containing 20 wt% AgI-MOR and 80 wt% glass with an additional 5wt% Ag flake added were heated to 550°C for 1 hr, the crystalline phase eulytite, $Bi_4(SiO_4)_3$ formed. The fact that the eulytite does not form with Ag-MOR implies that the AgI must be involved in the nucleation process. Fig. 4 shows that the degree for eulytite formation increased when the particle size of the AgI-MOR was smaller, <45 µm as opposed to <150 µm.

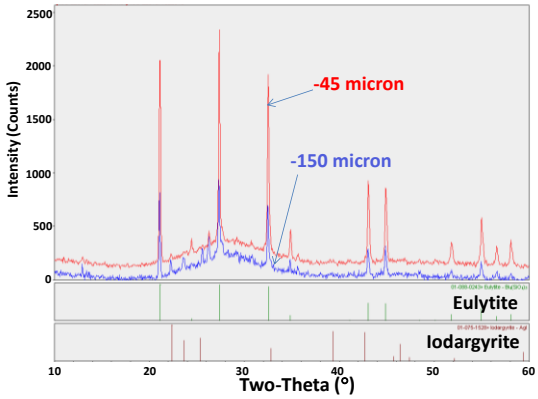

Fig. 4. XRD patterns for 20 wt% AgI-MOR samples heat treated at 550°C for 1 hr.

In situ XRD of the <45 µm sample indicated that the eulytite began to form after about 25 minutes at 550°C. SEM images of the sintered microstructures of samples with 15 wt% AgI-MOR with amorphous (550°C **for** 20 min) and crystalline (575°C for 1 hr) are shown in Figs. 5 and 6. The large dark regions in the micrographs are the mordenite and the eulytite particles are the brighter micron-size particles throughout the matrix phase.

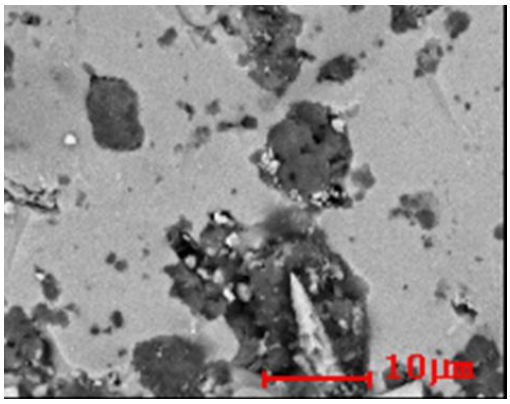

Fig. 5. SEM image of a 15 wt% AgI-MOR sample heated at 550°C for 20 min showing the amorphous glass phase.

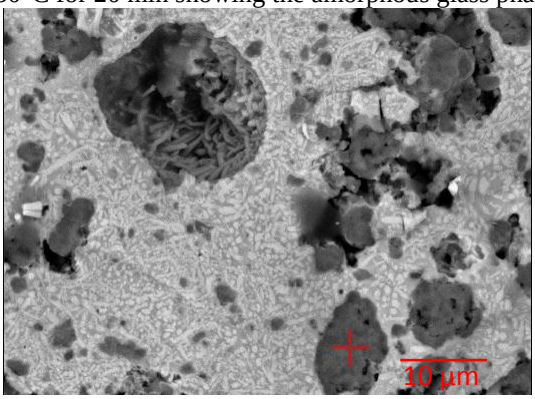

Fig. 6. SEM image of a 15 wt% AgI-MOR sample heated at 575°C for 1 hr min showing eulytite in the glass phase.

III.E. Waste Form Durability

Since the presence of eulytite could potentially affect the waste form durability, PCT and MCC-1 durability tests were performed on these amorphous (550°C for 20 min) and crystallized (575°C for 1 hr) samples with 15 wt% AgI-MOR. Both sets of samples had no open porosity and those for the PCT test were ground and sieved, while those for the MCC-1 test were ~1 cm diameter wafers with ground surfaces.

The results of the ICP-MS analysis of the leachates from the PCT and MCC-1 (average of three samples) are given in Tables 1 and 2, respectively. Although there is variation between the concentrations for the amorphous and crystallized samples, the values are comparable with Zn and Si having the highest concentrations and iodine having extremely low concentration in all cases. The SEM images of the surfaces of the MCC-1 pellets, shown

in Figs 7 and 8 both revealed needlelike bismuth oxide crystals, as identified by EDS.

TABLE I. PCT Leachate Results (ppm)

	Si	Bi	Zn	Al	I
Amorphous	20.3	0.021	14.6	0.234	0.002
Crystallized	18.4	0.064	98.7	0.494	0.001

TABLE 2. MCC-1 Leachate Results (ppm)

	Si	Bi	Zn	Al	I
Amorphous	38.3	0.10	75.2	6.0	0.0007
Crystallized	20.1	0.017	84.0	1.2	0.007

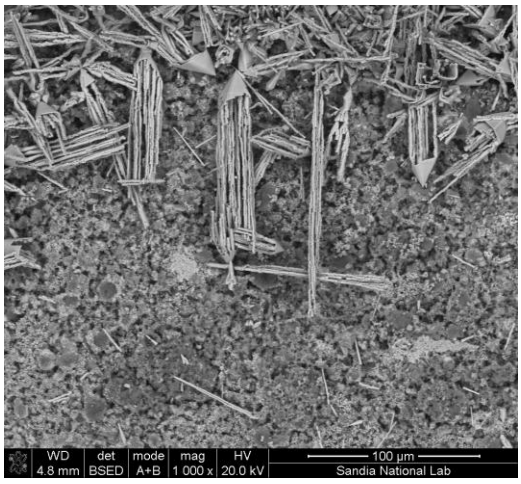

Fig. 7. SEM image of a 15 wt% AgI-MOR sample heated 550°C for 12 min after 7 days in water at 90°C.

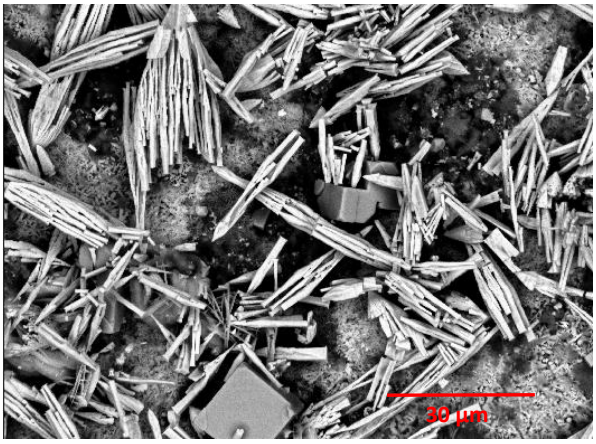

Fig. 8. SEM image of a 15 wt% AgI-MOR sample heated 575°C for 60 min after 7 days in water at 90°C.

IV. CONCLUSIONS

In this work, the processing and composition of durable glass composite waste forms for ^{129}I storage were investigated to optimize performance. The loading level of highly iodine-loaded AgI-MOR was increased to 25 wt% while maintaining high density (no open porosity) by heat treating at 625°C for 20 min. The amount of additional silver that must be added to react with any adsorbed iodine was determined to be 0.205 times the AgI-MOR loading level. The loss of AgI through volatilization during the heat treatment hold was determined to be only a small amount higher than what occurs during the baseline 550C for 1 hr treatment because the shorter time partly makes up for the higher AgI vapor pressure. Crystallization of the glass matrix to form eulytite can occur during the higher temperature heat treatment, but initial studies indicate that the presence of this phase does not negatively impact the good durability of the waste forms significantly.

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