Preparation of Hot Isostatically Pressed AgZ Waste Form Samples

Nuclear Technology Research and Development

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SUMMARY

The production of radioactive iodine-bearing waste forms that exhibit long-term stability and are suitable for permanent geologic disposal has been the subject of substantial research interest. One potential method of iodine waste form production is hot isostatic pressing (HIP). Recent studies at Oak Ridge National Laboratory (ORNL) have investigated the conversion of iodine-loaded silver mordenite (I-AgZ) directly to a waste form by HIP.

ORNL has performed HIP with a variety of sample compositions and pressing conditions. The base mineral has varied among AgZ (in pure and engineered forms), silver-exchanged faujasite, and silver-exchanged zeolite A. Two iodine loading methods, occlusion and chemisorption, have been explored. Additionally, the effects of variations in temperature and pressure of the process have been examined, with temperature ranges of 525°C–1,100°C and pressure ranges of 100–300 MPa. All of these samples remain available to collaborators upon request.

The sample preparation detailed in this document is an extension of that work. In addition to previously prepared samples, this report documents the preparation of additional samples to support stability testing. These samples include chemisorbed I-AgZ and pure AgI.

Following sample preparation, each sample was processed by HIP by American Isostatic Presses Inc. and returned to ORNL for storage. ORNL will store the samples until they are requested by collaborators for durability testing. The sample set reported here will support waste form durability testing across the national laboratories and will provide insight into the effects of varied iodine content on iodine retention by the produced waste form and on potential improvements in waste form durability provided by the zeolite matrix.

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ACRONYMS

AgA	silver-exchanged zeolite type A
AgX	silver-exchanged faujasite
AgZ	silver-exchanged mordenite
FY	fiscal year
HIP	hot isostatic pressing
I-AgZ	iodine-loaded silver-exchanged mordenite
NAA	neutron activation analysis
NaZ	sodium mordenite
ORNL	Oak Ridge National Laboratory
TGA	thermogravimetric analyzer

PREPARATION OF HOT ISOSTATICALLY PRESSED AGZ WASTE FORM SAMPLES

1. INTRODUCTION

The production of radioactive iodine-bearing waste forms that exhibit long-term stability and are suitable for permanent geologic disposal has been the subject of substantial research interest (Maddrell, 2005; Matyáš et al., 2011; Tanabe et al., 2010). The removal of volatile radioactive ^{129}I from the off-gas of a nuclear fuel reprocessing facility will be necessary to comply with the regulatory requirements that apply to facilities sited within the United States (Jubin et al., 2012), and any iodine-containing media or solid sorbents generated by off-gas abatement processes will require disposal.

One potential method of iodine waste form production is hot isostatic pressing (HIP). HIP, a common process, can be used to directly convert iodine-loaded sorbents to a durable waste form with little or no additional waste byproducts. In addition, HIP can provide substantial reductions in waste volume. Recent studies at Oak Ridge National Laboratory (ORNL) have investigated the conversion of iodine-loaded silver mordenite (I-AgZ) directly to a waste form by HIP (Bruffey and Jubin, 2015). Silver mordenite (AgZ), of the zeolite class of minerals, is under consideration for use in adsorbing iodine from nuclear reprocessing off-gas streams. Direct conversion of I-AgZ by HIP may provide the following benefits: (1) a waste form of high density that is tolerant to high temperatures, (2) a waste form that is not significantly chemically hazardous, and (3) a robust conversion process that requires no pretreatment.

ORNL has performed HIP on a wide variety of sample compositions (Bruffey, et al. 2016; Bruffey and Jubin, 2016). AgZ has been used in both pure and engineered forms, and alternative zeolites including silver-exchanged zeolite type A (AgA) and silver-exchanged faujasite (AgX) have been studied. The method of iodine inclusion has varied from occlusion (mixing and heating at high temperature to migrate iodine into the zeolite cage) to chemisorption from a gas stream, which is a process representative of off-gas treatment. Additionally, the effects of variations in the temperature and pressure of the process have been examined at temperature ranges of 525°C–1,100°C and pressure ranges of 100–300 MPa. Finally, the possibility of boosting mineral conversion through alumina addition to the sample material was explored. All of these samples remain available to collaborators upon request and are documented in Appendix A.

The sample preparation detailed in this document is an extension of that work. The effects of various sample compositions and pressing conditions can be assessed using density measurements, hardness measurements, and microscopic techniques, but ultimately, an optimized sample composition and pressing condition can only be determined through waste form stability testing. Both Argonne National Laboratory and Pacific Northwest National Laboratory are developing techniques to assess the stability of heterogenous iodine-containing waste forms (to include iodine-containing minerals) and will require prepared sample sets to conduct that testing. In addition to previous prepared samples, this report documents the preparation of additional samples to support stability testing. These samples include chemisorbed I-AgZ and pure AgI.

2. COMPREHENSIVE SAMPLE SET

Several variables can affect the properties of I-AgZ waste forms produced by HIP. The conditions of the pressing process itself (temperature, pressure, and hold time) are likely to have a large impact on the properties of the resultant waste form, in addition to any effects caused by variation in the I-AgZ starting materials (such as water content and iodine content). A sample set was designed so that the effects of each of these variables could be studied. In addition, the sample set was also intended to resolve an outstanding question identified during previous work about the natural variability of the waste forms produced by the

HIP process. This question was addressed by including replicate samples that were created using identical starting materials, sample preparation methods, and HIP conditions. Finally, the sample set included scaled-up samples to evaluate whether the method scaled as expected. The full sample set is shown in Table 1.

Table 1. Comprehensive sample set (grey indicates samples associated with this effort)

Sample	Temp. (°C)	Pressure (MPa)	Time (h)	Target iodine content (wt%)	Drying temp. (°C)	Characterization performed	Notes
1	700	100	3	100	None	Yes	
2	700	175	3	100	None	Yes	
3	700	175	3	100	None	Yes	
4	700	175	3	100	None	Yes	
5	700	300	3	100	None	Yes	
6	900	100	3	100	None	Yes	
7	900	175	3	100	None	Yes	
8	900	175	3	100	None	Yes	
9	900	175	3	100	None	Yes	
10	900	300	3	100	None	Yes	
11	1100	100	3	100	None	Yes	
12	1100	175	3	100	None	Yes	
13	1100	175	3	100	None	Yes	
14	1100	175	3	100	None	Yes	
15	1100	300	3	100	None	Yes	
16	900	175	6	100	None	Yes	
17	900	175	12	100	None	Yes	
18	525	100	3	100	None	Yes	
19	525	100	12	100	None	Yes	
20	900	175	3	100	150	Yes	
21	900	175	3	100	270	Yes	
22	900	175	3	100	450	Yes	
23	900	175	3	100	450	Yes	
24	900	175	3	100	450	No	Failed capsule
25	900	300	3	54	None	No	AgI powder
26	900	175	3	100	None	Yes	Scaled-up sample

Table 1. Comprehensive sample set (grey indicates samples associated with this effort) (continued)

Sample	Temp. (°C)	Pressure (MPa)	Time (h)	Target iodine content (wt%)	Drying temp. (°C)	Characterization performed	Notes
27	900	175	3	100	None	Yes	Scaled-up sample
28	900	175	3	100	None	Yes	Scaled-up sample
29	900	100	3	25	None	No	
30	900	175	3	25	None	No	
31	900	300	3	25	None	No	

A number of these samples were prepared and characterized by density measurement, optical microscopy and x-ray diffraction as part of a similar research effort. The samples prepared as part of the effort reported here were not characterized and are intended to be distributed in support of ongoing research efforts into the durability of heterogeneous iodine waste forms. Table 1 highlights the samples associated with this report.

3. SAMPLE PREPARATION

Two types of samples were prepared under this effort. The first includes samples that were prepared using AgZ sorbent that had been loaded with iodine to a target iodine content of 25 wt%. The second was a sample containing AgI powder.

3.1 Preparation of Sample Material

3.1.1 Iodine loading of AgZ

I-AgZ samples with a target iodine content of 25 wt% were prepared in a thermogravimetric analyzer (TGA). This type of thin bed iodine loading is described by Jubin (2011). Each sample was placed in a holder within an oven, where the weight of the sample was continuously measured to assess sorbent weight gain upon exposure to an iodine-bearing gas stream. A schematic of this system is shown in Figure 1. The general procedure for these tests was:

1) The sample was placed in the oven and exposed to a flowing stream of dry air (−70°C dew point) until fully equilibrated as measured by stable weight (±0.005 g/h).
2) The composition of the gas stream was modified with the addition of iodine at the desired concentrations while a constant total gas flowrate was maintained. The loading period lasted until the sorbent had increased in weight by 25%.
3) The gas stream was again modified to a dry air stream to remove physisorbed iodine.

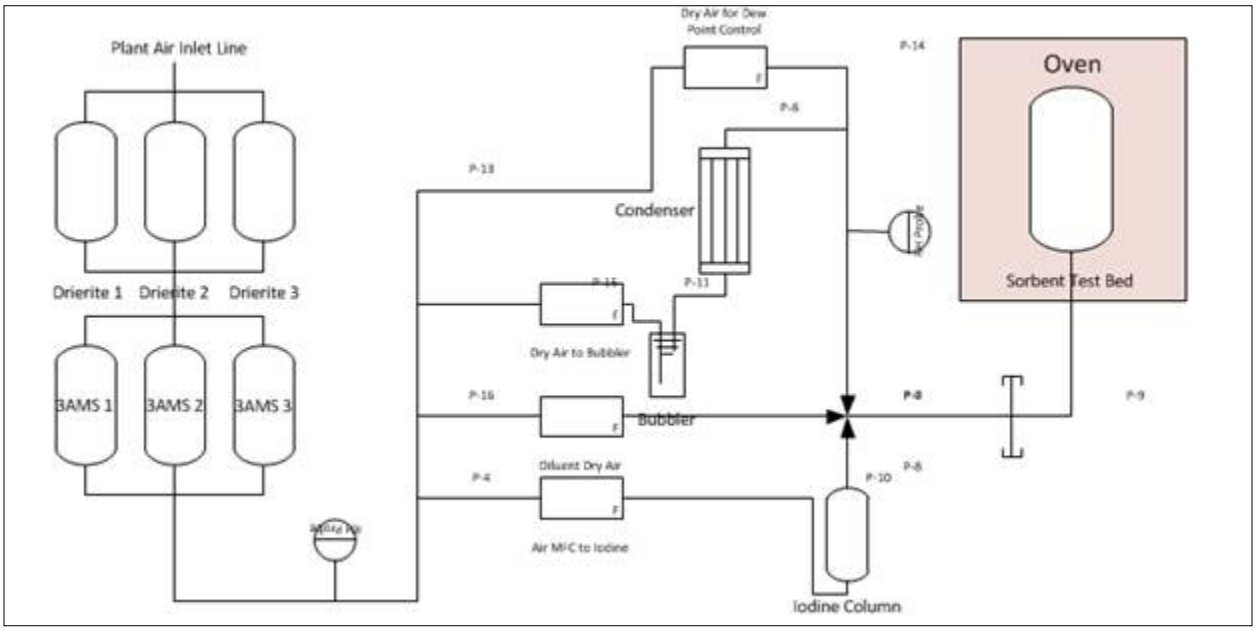

Figure 1. Schematic of TGA used for iodine loading of AgZ.

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16). It contains 11.9% silver by weight and has a pellet diameter of 1/16 in. Before use in this experiment, the material underwent a hydrogen reduction to reduce the silver incorporated in the material. The reduction was performed by drying a deep bed of AgZ at 270°C with a low flow of argon and then reducing the material for 10 days at 270°C with a gas mixture of 4% H_2/96% N_2.

AgZ was then loaded with iodine in a TGA using the method described above. The iodine concentration in the gas feed stream was 50 ppmv, and the water content was <3 ppmv. Iodine loading was conducted at 150°C with a constant superficial gas velocity of 10 m/min through the sample bed. After the sorbent had been loaded, a portion was sent for neutron activation analysis (NAA) to confirm total iodine content (Table 2). The estimated iodine content provided by the TGA can be affected by temperature, occasional balance instability, or other factors. For this reason, the iodine content is assumed to be more accurately measured by NAA.

Table 2. Iodine content of partially loaded samples

Sample ID	TGA iodine content estimate (mg/g AgZ)	NAA iodine content measurement (mg/g AgZ)
29	25	32
30	22	34
31	28	47

3.1.2 Powder source materials

AgI powder (99.999% pure, metals basis) was purchased from Alfa Aesar and used directly.

3.2 Capsule Design, Loading, and Sealing

Each sample was emplaced into sample capsules with an outer diameter of 3/4 in. Each capsule was 1 in. long, resulting in an internal volume of 6.3 cm^3. The sample capsules were constructed of 304 stainless

steel tubing. The wall thickness of the tubing and the end cap was 0.020 in. Each end cap consists of a slightly inset lid with a vent port constructed of 1/16 in. stainless steel tubing. A sealed capsule is shown in Figure 2.

Figure 2. Sealed sample capsule.

In the case of samples consisting of pelletized I-AgZ, roughly 5 g of material was poured into the capsules and briefly shaken to ensure even packing. There was a gap of 1/8 in. in length between the material and the capsule lid. For Sample 25, the AgI powder (8 g) was also gently poured in and packed by gentle tapping. The lid was then sealed into place by electron beam welding, which is performed under vacuum.

4. HIP AND PATH FORWARD

The samples were processed using HIP by American Isostatic Presses Inc. according to the conditions provided in Table 1 and then returned to ORNL. ORNL will store the samples until they are requested by collaborators for durability testing. A representative sample is shown in Figure 3. A scaled-up sample is included for comparison.

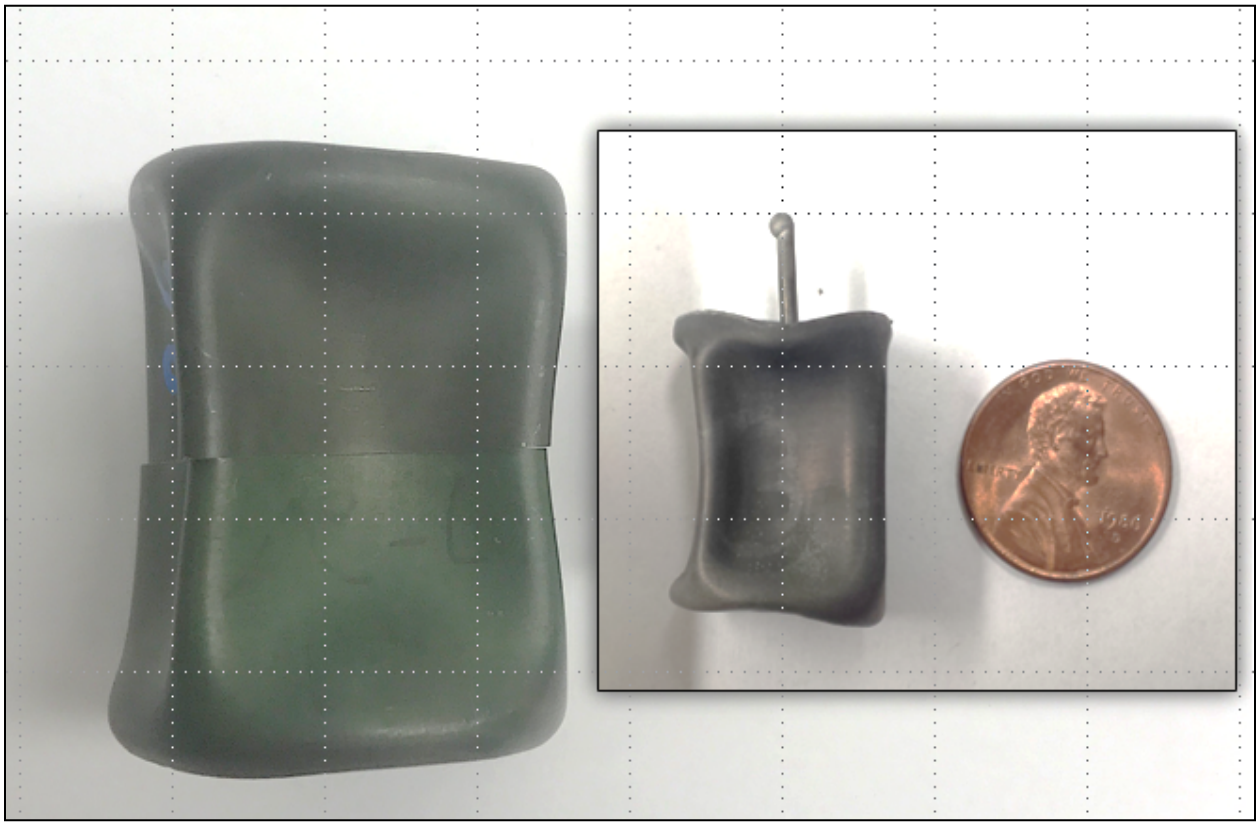

Figure 3. Pressed I-AgZ waste forms. *Right*, original capsule. *Left,* scaled-up capsule.

One of the most important samples is Sample 25, which consists of AgI powder. This sample can be used as a baseline in durability testing to determine whether the silver mordenite matrix adds additional durability or resistance to waste form dissolution beyond that of AgI, a compound already characterized as having very low solubility in aqueous media. The other samples in this sample set will also continue to support waste form testing across the national laboratories and will provide insight into the effects of varied iodine content on iodine retention by the produced waste form.

5. REFERENCES

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APPENDIX

Table A1. HIP samples available for testing (prepared in fiscal year [FY] 2015)

Sample	Temperature (°C)	Pressure (MPa)	Particle form and volume ratio	Notes
2-1	525	175	NaZ Powder + AgI (3:1)	Pure zeolite
2-2	700	175	NaZ Powder + AgI (3:1)	Pure zeolite
2-3	900	175	NaZ Powder + AgI (3:1)	Pure zeolite
2-4	700	175	NaZ Powder + AgI (6:1)	Pure zeolite
2-5	900	175	NaZ Powder + AgI (6:1)	Pure zeolite
2-6	700	300	NaZ Powder + AgI (6:1)	Pure zeolite
2-7	700	300	NaZ Powder + AgI (3:1)	Pure zeolite
2-11	900	100	NaZ Powder + AgI (3:1)	Pure zeolite
2-12	900	175	Ground Ag°Z + AgI (3:1)	Engineered zeolite
2-13	900	175	Ground Ag°Z + AgI (6:1)	Engineered zeolite
2-16	900	175	Ground Ag^0Z loaded with I	
2-17	900	175	Ground Ag^0Z loaded + NaZ powder (1:2)	
2-21	1100	175	NaZ Powder + AgI (3:1)	Pure zeolite
2-23	900	175	NaZ Powder + NaI (3:1)	Pure zeolite
2-24	900	175	NaZ Powder + NaI (6:1)	Pure zeolite

Table A2. HIP samples available for testing (prepared in fiscal year [FY] 2016)

Sample ID	Mineral form	Method of iodine inclusion	Molar ratio (zeolite:AgI)	Alumina	Pressure (MPa)
FY16-HIP-**1**	AgA	Occlusion	1:2.0	No	190
FY16-HIP-**2**	AgA	Occlusion	1:2.0	No	300
FY16-HIP-**3**	NaZ	Occlusion	1:2.5	No	300
FY16-HIP-**4**	NaZ	Occlusion	1:1.3	No	300
FY16-HIP-**5**	AgZ	Occlusion	1:2.6	No	300
FY16-HIP-**6**	AgZ	Occlusion	1:1.4	No	300
FY16-HIP-**7**	AgX	Occlusion	1:14.7	No	300
FY16-HIP-**8**	AgX	Occlusion	1:14.8	No	300
FY16-HIP-**9**	AgA	Chemisorption	1:0.2	No	175
FY16-HIP-**10**	AgA	Chemisorption	1:0.2	No	300
FY16-HIP-**11**	AgZ	Chemisorption	1:0.2	No	175
FY16-HIP-**12**	AgZ	Chemisorption	1:0.2	No	300
FY16-HIP-**13**	AgX	Chemisorption	1:2.8	No	175
FY16-HIP-**14**	AgX	Chemisorption	1:2.8	No	300
FY16-HIP-**15**	AgZ	Chemisorption	1:0.2	Yes	300
FY16-HIP-**16**	AgX	Chemisorption	1:2.8	Yes	300