High-Temperature Pressing of Silver-Exchanged Mordenite into a Potential Iodine Waste Form – 14096

Robert T. Jubin *, Stephanie H. Bruffey *
*Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831

ABSTRACT

Extensive work is currently under way to evaluate silver-exchanged mordenite (AgZ) as a capture media for the iodine released to the off-gas streams during the reprocessing of used nuclear fuel. Recent work at ORNL has been conducted to determine if hot isostatic pressing (HIPing) could be an effective method for the direct conversion of iodine-loaded reduced silver-exchanged mordenite (I-Ag^0Z) into a suitable waste form. The high temperatures and pressures exerted on a material during HIPing have been demonstrated to successfully convert krypton- and chlorine-bearing materials into waste forms of high density. The minimal pretreatment required for HIPing makes this a potentially attractive and economically desirable method for waste form production.

In the late 1970s and early 1980s, Idaho National Laboratory (INL) examined the technical feasibility of immobilizing krypton-85 in a zeolite structure produced by HIPing. The zeolite was sintered at 700°C and 100 MPa for 2 to 4 hours. Work at Argonne National Laboratory (ANL) and INL to develop a waste form for the E-chem process utilized a glass frit and zeolite loaded with fission products. This mixture was hot isostatic pressed (HIPed) at temperatures of 700 to 750°C and pressures of 41 to 172 MPa. The National Nuclear Laboratory in the United Kingdom has demonstrated HIPing of A and X zeolites at 900°C, converting them to a sodalite. In Japan, work has been conducted on the sintering of silver nitrate–impregnated silica gel (AgS). The material was sintered at 700°C and 100 MPa. Silver nitrate–impregnated alumina (AgA) was also sintered at 850°C and 175 MPa.

In the initial stages of this work, the use of hot uniaxial pressing (HUPing) to prepare samples of reduced silver-exchanged mordenite (Ag^0Z) was assessed, and the resulting product of the process was evaluated. The starting material was fresh Ag^0Z with a bulk density of 0.77 g/cm^3. The first pressed sample consisted of the engineered pelletized form produced by the manufacturer, and the second sample consisted of the same material that had been crushed using a mortar and pestle. The pressing was conducted at ~27.5 MPa at 750°C for 1 hour.

A second phase of scoping tests was conducted to evaluate the benefits of the higher pressure that could be achieved by HIPing. The initial temperature range of interest was 525 to 900°C, and the pressure ranged from 41 to 175 MPa. The test structure was designed to determine the effect of pressure and temperature variations and the need to crush the Ag^0Z pellets prior to HIPing. Additionally, samples of I-Ag^0Z were also pressed, providing insight into the effects of

iodine on the resulting product and whether there was any migration of iodine within the product. The densities of the compacts resulting from HIPing are significantly higher than those from HUPing. Based on product density, there was no obvious advantage to crushing the sample prior to HIPing or HUPing. At 175 MPa the density of the AgZ was determined to be 2.60 to 2.65 g/cm^3. This is an increase in density of ~340% over the bulk density of the starting material. The samples are now undergoing destructive analysis.

INTRODUCTION

The purpose of this project was to determine if hot isostatic pressing (HIPing) could be a worthwhile method for direct conversion of iodine-loaded reduced silver-exchanged mordenite (I-Ag^{0}Z) into a suitable waste form. The high temperatures and pressures exerted on a material during HIPing have been demonstrated to successfully convert krypton- and chlorine-bearing materials into waste forms of high density [1]. The minimal pretreatment required to prepare I-Ag^{0}Z for HIPing makes this an attractive and economically desirable method for waste form production.

LITERATURE REVIEW

In the late 1970s and early 1980s INL examined the technical feasibility of immobilizing krypton-85 in a hot isostatic pressed (HIPed) zeolite structure. No additional binder material was added, and the zeolite was sintered at 700°C and 100 MPa for 2 to 4 hours [1]. Loading of 30 to 60 m³ of krypton per cubic meter of solid was possible. The product was amorphous and krypton leakages were very low at temperatures up to 750°C.

Work at ANL [2] and the INL [3] to develop a waste form for the E-chem process utilized a glass frit and zeolite loaded with fission products. This mixture was HIPed at temperatures of 700 to 750°C and pressures of 41 to 172 MPa. The zeolites included 3A, 4A, and 5A forms and contained 21 wt% salt mixed with up to 45% glass frit. A pressureless version involved heating the material to 925°C.

The National Nuclear Laboratory in the United Kingdom has demonstrated HIPing of A and X zeolites at 900°C, converting them to a sodalite [4].

In Japan, work has been conducted on the sintering of silver nitrate–impregnated silica gel (AgS) [5]. In this work, the particle size was 45 µm and no additional material was added. The material was sintered at 700°C and 100 MPa for 3 hours. Silver nitrate–impregnated alumina (AgA) was also sintered at 850°C and 175 MPa for 3 hours.

EXPERIMENTAL

In this work, an initial attempt assessed the use of hot uniaxial pressing (HUPing) to prepare two pressed samples of non-iodine-loaded reduced silver exchanged mordenite (Ag^{0}Z) and evaluated the resulting product. The starting material was fresh Ag^{0}Z with a bulk density of 0.77 g/cm^3. The first pressed sample consisted of the engineered pelletized form produced by the manufacturer, and the second sample consisted of the same material that had been crushed using a mortar and pestle. No sieving was performed on the crushed material used in test conducted in the hot uniaxial press (HUP), as shown in Figure 1. The cover gas was argon at

10 in. of Hg, and the pressing was conducted at ~4000 psi (~27.5 MPa) at 750°C for 1 hour. The furnace and press are shown in Figure 2. Figures 3 and 4 show the resulting compacts from intact Ag^0Z pellets and from crushed Ag^0Z. Figure 5 shows the cross section of the compact pressed from the pelletized form of Ag^0Z.

An attempt was made to determine the crush strength of the resulting compact. However, one-half of the sectioned compact was placed between two gauge blocks, and as soon as the handle of the gauge was moved, the pellet fractured. No recording was made of the pressure. The fractured compact is shown in Figure 6.

The properties of the hot uniaxial pressed (HUPed) pellets are shown in Table I. Minimal weight loss (<50 mg) was observed for these compacts, but the AgZ contained no iodine. Weight loss might be expected from either the loss of water contained within the mordenite or from the volatilization of small amounts of iodine, if present. The loss of iodine is of primary concern, as the melting point of AgI (the expected chemical form of iodine) is only 558°C and HUP temperature was 750°C. However, the boiling point of AgI is 1506°C and only limited volatilization should be expected. The bulk volume of the Ag^0Z was reduced in both samples by ~50%.

Figure 1. Crushed Ag^0Z used in HUP testing.

Figure 2. Hot uniaxial press and furnace used in initial testing for Ag^0Z pressing.

Figure 3. HUPed compacts from pellet form Ag^0Z (left) and crushed Ag^0Z (right).

Figure 4. Side view of HUPed compacts from pellet form Ag^0Z (left) and crushed Ag^0Z (right).

Figure 5. Cross section of HUPed compact from pellet form Ag^0Z.

Figure 6. Crushed HUPed compact formed from pellet form Ag^0Z.

TABLE I. Physical property data on HUPed Ag^0Z compacts

	Crushed Ag^0Z	**Pellet form Ag^0Z**
Diameter (in.)	0.506	0.510
Height (in.)	0.703	0.705
Final Weight (g)	3.0150	3.0926
Density (g/cm^3)	1.29	1.30

The pressures used in this HUPing were relatively low compared to the pressures used in previously reported HIPing of either Kr-85 loaded zeolite 5A, which was conducted at 700°C and 100 MPa for 2 to 4 hours, or several iodine waste forms that were pressed at temperatures ranging from 700 to 900°C and pressures from 100 to 175 MPa.

To evaluate the benefits of the higher pressure that could be achieved by HIPing, a contract was placed with a commercial vendor, American Isostatic Presses, Inc. (AIP), for a second phase of scoping tests. The test matrix is laid out in Table II. The initial temperature range of interest was 525 to 900°C and with a pressure range of 41 to 175 MPa.

The test regime was designed to determine the effect of pressure and temperature variations on pellet size. Additionally, samples of $I\text{-}Ag^0Z$ were also pressed, providing insight into the effects of iodine presence on pressing and whether there is any migration of iodine as a result of different temperatures involved in the pressing process.

Samples 1, 2, 3 examine the impact of the hot isostatic press (HIP) pressure
Samples 2, 4, and 5 evaluate variations in HIP temperature
Samples 2 and 6 compare the need for size reduction of the Ag^0Z pellets
Samples 3 and 8 compare the presence of iodine on the Ag^0Z
Samples 7 and 8 compare temperature on possible iodine/silver migration

TABLE II. Proposed test matrix

Sample	Temperature (°C)	Pressure (MPa)	Time (hr)	Particle form
1	700	50	3	Intact Ag^0Z
2	700	100	3	Intact Ag^0Z
3	700	175	3	Intact Ag^0Z
4	525	100	3	Intact Ag^0Z
5	850	100	3	Intact Ag^0Z
6	700	100	3	Crushed Ag^0Z
7	525	175	3	Intact Ag^0Z-I
8	700	175	3	Intact Ag^0Z-I

The sample containers were constructed of 304 stainless steel tubing, and each contained approximately 5 g of Ag^0Z or I-Ag^0Z. The wall thickness was 0.020 in., and the end caps were 0.010 in. thick. The capsules were sealed using electron beam welding in a vacuum chamber. During the electron beam welding, Capsule #1 failed due to a failed electron beam weld on one end of the capsule during final closure and the sample leaked. Figures 7 and 8 show a representative sample capsule prior to pressing. Table III shows the sample and container weights.

TABLE III. Samples prepared for initial Ag^0Z HIPing tests

Sample	Contents	Sample weight (g)	Weight of welded can containing sample (g)	Notes
1	Ag^0Z	5.0483	13.1002	Leaker
2	Ag^0Z	5.2936	13.4354	
3	Ag^0Z	4.9452	12.9701	
4	Ag^0Z	5.4169	13.6007	
5	Ag^0Z	4.6740	12.6897	
6	CrushedAg^0Z	5.0181	13.0440	
7	I_2-Ag^0Z	4.9836	12.8954	
8	I_2-Ag^0Z	5.2735	13.3513	

The seven remaining sample capsules were shipped to AIP in early July to perform the HIPing. AIP conducted the pressing of the samples during the period of July 8–15 and then returned the capsules to ORNL for analysis. Figures 9, 10, and 11 show a representative post-pressing sample.

Figure 7. End of I-Ag^{0}Z loaded capsule No. 8.

Figure 8. Side view of I-Ag^{0}Z loaded capsule No. 8.

The density of the resulting product in the returned samples was determined. This was accomplished by determining the volume of the “crushed” container by volume displacement

using a graduated cylinder. The volume of the stainless steel used to form the capsule was assumed to be unaffected by the HIPing, and the volume was calculated based on the weight of the stainless steel in each original capsule using a density of 8.03 g/cm³. Table IV shows the resulting densities of the HIPed samples. The densities resulting from HIPing are significantly higher than those from the hot uniaxial pressing. The densities also show a direct correlation between the HIP pressure and the HIP temperature. There was no obvious advantage in regards to density for crushing of the sample prior to HIPing. The samples are now undergoing destructive analysis. This will include cutting open the sample, scanning electron microscopy of the cross-sectioned surface, and X-ray diffraction to determine the resulting phases present in the pressed sample. Analysis of the silver and iodine distributions within the resulting product will also be determined.

At 175 MPa the calculated density of the AgZ was 2.6–2.65 g/cm^3. This is an increase in density of ~340% over the bulk density of the starting material. At 100 MPa the density was increased by ~275% with the one exception of the sample that was pressed at 850°C, which also achieved a density of ~ 2.6 g/cm^3. This is a significant increase in sample density over those that were HUPed in which the density was increased by only 170%.

Figure 9. HIPed capsule containing Ag^{0}Z.

Figure 10. HIPed capsule containing I-Ag^{0}Z.

Figure 11. HIPed capsule containing I-Ag^{0}Z.

TABLE IV. Density of AgZ samples from initial HIPing tests

Sample	Temperature (°C)	Pressure (MPa)	Time (hr)	Particle form	Density (g/cm^3)
~~1~~ (leaker) skip test	~~700~~	~~50~~	~~3~~	~~Intact Ag^0Z~~	
2	700	100	3	Intact Ag^0Z	2.12
3	700	175	3	Intact Ag^0Z	2.65
4	525	100	3	Intact Ag^0Z	1.95
5	850	100	3	Intact Ag^0Z	2.62
6	700	100	3	Crushed Ag^0Z	2.06
7	525	175	3	Intact I- Ag^0Z	2.62
8	700	175	3	Intact I-Ag^0Z	2.50

Figures 12 and 13 show the cross sections for HIPed Ag^0Z samples 2 and 3. These were both HIPed at 700°C but at different pressures. No obvious differences were observed at this resolution even though the density of sample 3 was higher. Figure 14 is a cross section of capsule 6 which contained crushed AgZ. This was HIPed under the same conditions as capsule 2, which contained intact AgZ (Figure 12). Figure 15 is a cross section of capsule 8, which contained iodine-loaded AgZ. This capsule was HIPed under the same conditions as sample 3 (Figure 13). This cross section shows a marked change in the color of the compressed material.

Figure 12. Cross section of HIPed sample 2 (700°C and 100 MPa).

Figure 13. Cross section of HIPed sample 3 (700°C and 175 MPa).

Figure 14. Cross section of HIPed sample 6 (crushed AgZ, 700°C and 100 MPa).

Figure 15. Cross section of HIPed sample 8 containing I-AgZ (700°C and 175 MPa).

CONCLUSIONS

The purpose of this scoping project was to determine if hot isostatic pressing (HIPing) could directly convert iodine-loaded silver-exchange mordenite (I-AgZ) into a suitable waste form. The initial attempt was to evaluate the use of hot uniaxial pressing (HUPing) to prepare samples of non-iodine-loaded silver exchanged mordenite (AgZ) and to evaluate the resulting products. The resulting samples were very fragile due to the low pressure (~ 28 MPa) used. The second phase of tests focused on increasing the pressure up to 175 MPa using a commercial vendor to perform the HIPing of samples prepared at ORNL.

The densities of the compacts resulting from HIPing are significantly higher than those from the HUPing. There was no obvious advantage, density-wise, for the crushing of the sample prior to HIPing or HUPing. At 175 MPa the calculated density of the AgZ was 2.6 to 2.65 g/cm^3. This is an increase in density of ~340% over the bulk density of the starting material. At 100 MPa the density was increased by ~275% with the one exception of the sample that was pressed at 850°C, which also achieved a density of ~ 2.6 g/cm^3. This is a significant increase in sample density over those that were HUPed in which the density was increased by only 170%. This can be directly attributed to the lower pressures used in the HUPing tests.

REFERENCES

1. A. B. CHRISTENSEN, J. A. DEL DEBBIO, D. A. KNECHT, J. E. TANNER, and S. C. COSSEL, “Immobilization of krypton 85 in zeolite5A,” *Proceedings of the 17th DOE Nuclear Air Cleaning Conference*, CONF-820833, pp. 183–197, 1983.

2. C. PEREIRA, M. HASH, M. LEWIS, and M. RICHMANN, “Ceramic-Composite Waste Forms from the Electrometallurgical Treatment of Spent Nuclear Fuel,” *Journal of Materials*, 34–40, July 1997.

3. STEPHEN PRIEBE and KEN BATEMAN, “The Ceramic Waste Form Process at Idaho National Laboratory,” *Nuclear Technology*, 199, 207 (162), May 2008.

4. EWAN MADDRELL, “Capture and Immobilization of Iodine,” National Nuclear Laboratory, November 2, 2005.

5. TSUTOMU NISHIMURA, TOMOFUMI SAKURAGI, YUJI NASU, HIDEKAZU ASANO, and HIROMI TANABE, “Development of immobilization techniques of radioactive iodine for geological disposal,” Mobile Fission and Activation Products in Nuclear Waste Disposal, January 16–19, 2007, mofap07.in2p3.fr/17janvier/Mofap07%20OHP%20T.pdf