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Recommend HIP Conditions for AgZ

Fuel Cycle Research & Development

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SUMMARY

Reduced silver-exchanged mordenite (Ag^0Z) is being evaluated as a potential material to control the release of radioactive iodine into the plant off-gas streams during the reprocessing of used nuclear fuel. After iodine has been adsorbed and immobilized as AgI, the sorbent must then be disposed of as high level waste. Recent work has examined the potential of hot isostatic pressing (HIPing) as a method to directly convert iodine-loaded reduced silver-exchanged mordenite ($I\text{-}Ag^0Z$) into a suitable waste form (Bruffey et al., 2014). Direct conversion with minimal pretreatment of the waste, as could be provided by HIPing, is an economically desirable pathway that can minimize radiological handling concerns.

One goal of this work has been to transform the component material into a well-characterized iodine-containing mineral phase. This would limit the additional experimental testing and modeling required to determine the long-term stability of the pressed pellet, as much of that information has already been learned for several common iodine-containing minerals.

The purpose of this study was to continue research to determine if HIPing could directly convert $I\text{-}Ag^0Z$ into a suitable waste form. Fiscal year (FY) 2015 work completed studies of Phase IIA, IIB, and IIC samples. Product consistency testing (PCT) of Phase IIA samples resulted in iodine release below detection limit for six of twelve samples. This is promising and indicates that a durable waste form may be produced through HIPing even if transformation of the zeolite to a distinct mineral phase does not occur. From PCT results of Phase IIA samples, it was determined that future pressing should be conducted at a temperature of 900°C.

Phase IIC testing continued production of samples to examine the effects of multiple source materials, compositional variations, and an expanded temperature range. The density of each sample was determined and x-ray diffraction (XRD) patterns were obtained. In all cases, there was nothing in the XRD analyses to indicate the creation of any AgI-containing silicon phase; the samples were found to be largely amorphous.

Each sample is prepared by encapsulation of the material in a stainless steel capsule. Progress was impaired due to multiple capsule failures throughout the year. Mitigation of capsule failures will be a critical component to the success of continued work. It is believed that the source of these failures could be three-fold: (1) welding issues, (2) generation of water vapor in the sample during pressing, and (3) density change from the packed powder to final form was too large, leading to excessive capsule deformation.

To continue the fundamental research and development into this process, the set of samples will be prepared, pressed and analyzed. These samples will be prepared utilizing lessons learned from previous capsule failures. First, samples correlating to the work performed by Sheppard (2006) that resulted in the formation of sodalite will be prepared to demonstrate a baseline production method. Second, samples of AgZ either occluded with or containing chemisorbed iodine will be processed according to similar pressing conditions. Finally, the use of alumina as an additive to promote sodalite formation will be investigated. The results from these samples and from earlier work will be used to further refine the envelope of pressing conditions for engineered silver mordenite or other silver zeolites as research moves toward scaling up of sample size.

There is concern that PCT is not suitable for the determination of long-term stability of heterogeneous waste forms such as those that are produced by HIP. Other testing methods will be considered and initiated in collaboration with waste form experts as appropriate. The ultimate goal of investigations into HIPing of $Ag^0Z\text{-}I$ is to produce a pellet that can be demonstrated to have high iodine retention and that is considered to be a promising candidate for long-term stability and disposition of iodine-containing zeolite sorbents.

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ACRONYMS

AgZ	Silver-exchanged mordenite
Ag^0Z	Reduced silver-exchanged mordenite
FY	fiscal year
HIP	Hot Isostatic Pressing
HUP	Hot Uniaxial Pressing
I-Ag^0Z	Iodine-loaded reduced silver-exchanged mordenite
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ORNL	Oak Ridge National Laboratory
PCT	Product Consistency Testing
SEM-EDS	Scanning Electron Microscopy-Electron Dispersive Spectroscopy
XRD	X-ray Diffraction

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

RECOMMEND HIP CONDITIONS FOR AgZ

1. INTRODUCTION

Reduced silver-exchanged mordenite (Ag^0Z) is being evaluated as a potential material to control the release of radioactive iodine during the reprocessing of used nuclear fuel into the plant off-gas streams. After iodine has been adsorbed and immobilized as AgI, the sorbent must then be disposed of as high level waste. Recent work has examined the potential of hot isostatic pressing (HIPing) as a method to directly convert iodine-loaded reduced silver-exchanged mordenite ($I\text{-}Ag^0Z$) into a suitable waste form (Bruffey et al., 2014). Direct conversion with minimal pretreatment of the waste, as could be provided by HIPing, is an economically desirable pathway that can minimize radiological handling concerns.

One goal of this work has been to transform the component material into a well-characterized iodine-containing mineral phase. This would limit the additional experimental testing and modeling required to determine the long-term stability of the pressed pellet, as much of that information has already been learned for several common iodine-containing minerals.

Determination of pressing conditions was guided by a literature review of similar studies. The limited amount of information available indicates that this is a novel approach to iodine waste form production. Some results from this literature survey were discussed by Bruffey et al. (2014), and summaries of several additional studies are provided here, with full details found in Jubin and Bruffey, 2015.

HIPing has been explored by multiple researchers as an option for direct conversion of AgI-zeolites. A Japanese and U.S. patent provides a method for the HIPing of iodine-loaded silver zeolite or silver silica gel with a metal (Fukumoto, 1998). These studies used a 50:50 mix of an X-type silver-exchanged zeolite sorbent and copper powder HIPped at 860°C at 19 MPa for 3 h.

Hot uniaxial pressing (HUPing) and HIPing of iodine-loaded silver alumina sorbents in Pb–Fe-phosphate glass was studied by Perera et al. (2004). The loaded glass was ground to a fine powder and was HIPped at 500°C and 100 MPa for 1 h.

Sheppard et al. (2006) investigated the conversion of various AgI–zeolites (including the forms A, X, and Y) to form sodalite. Silver zeolites A and X appear to form monolithic sodalities when occluded with AgI at 400°C and then subsequently HIPed at 900°C at 190 MPa for 2 h.

Although a number of studies have been conducted on iodine-loaded silver-exchanged or -impregnated sorbents, we have not found any studies on the direct HIPing of iodine-loaded silver mordenite, currently under consideration as a capture material for iodine from the off-gas streams in a fuel reprocessing plant.

One possible objective of this effort is to form iodine sodalite from iodine-loaded mordenite or other zeolite by HIPping. Leach tests of iodide and iodate sodalite results indicate that they may have sufficiently low dissolution rates to limit the release to that required for a long-term waste form (Strachan and Babad, 1979). Table 1 shows the chemical formulas for four common zeolites along with sodalite.

Table 1: Zeolite formula

Zeolite framework	Typical formula	Si:Al ratio
Z (Mordenite)	$M_8^+(Al_8Si_{40}O_{96}) \cdot 24H_2O$	5:1
X	$M_{86}^+(Al_{86}Si_{106}O_{384}) \cdot 264H_2O$	1.23:1
Y	$M_{56}^+(Al_{56}Si_{136}O_{384}) \cdot 250H_2O$	2.43:1
A	$M_{12}^+(Al_{12}Si_{12}O_{48}) \cdot 27H_2O$	1:1
Sodalite	$M_6^+(Al_6Si_6O_{24}) \cdot (M^+X^-)_2$	1:1

Sheppard et al. (2006) shows proposed conversion pathways for zeolites A, X, and Y to sodalite as shown in Eqs. (1–3).

Zeolite A

$$M_{12}^+(Al_{12}Si_{12}O_{48}) \cdot 27H_2O + 4\,AgI \rightarrow 2[M_6^+(Al_6Si_6O_{24}) \cdot 2(AgI)] + 27H_2O \quad \textbf{(1)}$$

Zeolite X

$$3[M_{86}^+(Al_{86}Si_{106}O_{384}) \cdot 264H_2O] + 86\,AgI \rightarrow 43[M_6^+(Al_6Si_6O_{24}) \cdot 2(AgI)] + 60SiO_2 + 792H_2O \quad \textbf{(2)}$$

Zeolite Y

$$3[M_{56}^+(Al_{56}Si_{136}O_{384}) \cdot 250H_2O] + 56\,AgI \rightarrow 28[M_6^+(Al_6Si_6O_{24}) \cdot 2(AgI)] + 240SiO_2 + 750H_2O \quad \textbf{(3)}$$

Based on these three reactions from Sheppard, we are proposing a similar reaction for mordenite:

Zeolite Z

$$3[M_8^+(Al_8Si_{40}O_{96}) \cdot 24H_2O] + 8\,AgI \rightarrow 4[M_6^+(Al_6Si_6O_{24}) \cdot 2(AgI)] + 96SiO_2 + 72H_2O. \quad \textbf{(4)}$$

The proposed reactions for zeolite A, X, Y show an increase in the ratio of SiO_2 to sodalite (Table 2).

Table 2: SiO_2 to sodalite ratio for selected conversions

Precursor to sodalite	SiO_2 to sodalite ratio
A	0:1
X	1.40:1
Y	8.57:1
Mordenite (Z)	24:1

Sheppard et al. (2006) suggest that it is likely that the iodine-loaded zeolites X and Y would form silicon-rich phases as shown in Table 2. In that study, sodalite was not observed for the HIPed zeolite Y. By analogy, this suggests that mordenites will form an amorphous material with a significant silicon-rich phase and that little or no sodalite will form.

The objective of this report is to describe the work conducted on the HIPing of I-Ag^0Z in fiscal year (FY) 2015 and to recommend HIPing conditions for tests to be conducted in FY 2016. Testing has been

conducted in phases, with scoping tests and Phase I testing completed in FY 2014, Phase IIA and IIB testing conducted in FY 2014-FY 2015, and Phase IIC conducted in FY 2015. Scoping tests examined whether HUPing could be used to produce a waste form. Results from this testing indicated that the higher pressures and temperatures of HIPing would be required. Phase I studied the pressing of engineered Ag^0Z under a wide suite of pressing conditions and temperatures to begin understanding the effects of these parameters on the resultant waste form. Phase IIA and IIB investigated pressing of samples containing iodine (as AgI or NaI), pure sodium mordenite and engineered silver mordenite. Phase IIC investigated the pressing of pure silver-exchanged mordenite that contained iodine either as chemisorbed AgI or mixed with the mordenite powder. The goal of FY 2016 work is to complete fundamental research and development on this process and to initiate scale-up in sample size.

2. MATERIALS AND METHODS

Sodium iodide powder (99.9% pure, metals basis) and silver iodide powder (99.999% pure, metals basis) were purchased from Alfa Aesar. Synthetic sodium mordenite powder was manufactured by Wako Chemicals. Silver mordenite powder was produced at Oak Ridge National Laboratory (ORNL) by ion exchange of the sodium mordenite powder.

Engineered, pelletized silver mordenite (Zeolon 900) was obtained from Molecular Products (Ionex-Type Ag 900 E16) and is shown in Figure 1. It contained 9.5% silver by weight and has 1/16 in. pellet diameter. Prior to use in this experiment, the material underwent a hydrogen reduction to form Ag^0Z. The reduction was performed at 270°C for 10 d as described in Anderson, 2012.

Production of iodine-loaded engineered AgZ (AgZ-I) or Ag^0Z (Ag^0Z-I) was performed in a thermogravimetric analyzer as detailed in Jubin, 2011.

Figure 1. Engineered silver mordenite supplied by Molecular Products.

The sample capsules were constructed of 304 stainless steel tubing. The wall thickness was 0.020 in., and the end caps were 0.010 in. thick. The internal volume was estimated to be 6.5 cm^3. The capsules were filled with the sample material according to the prescribed test matrix. The capsules were sealed using electron beam welding in a vacuum chamber. The filled and sealed capsules were then sent to a commercial vendor, American Isostatic Presses, Inc., to conduct the HIPing according to the specified temperature and pressure desired for each individual capsule.

X-ray diffraction (XRD) patterns were collected by performing continuous θ-2θ scans on a Panalytical X'pert diffractometer from nominally 5 to 90° 2θ using CuKα radiation (λ = 1.540598 Å) and a X'Celerator detector. All scans used ¼°fixed slits, ½°anti-scatter slit and 0.04 soller slits coupled with a 10 mm mask (beam length). For the phase identification procedure, a search match was conducted using the Jade software (Jade, 2012) with the ICDD database (ICDD, 2013).

Product consistency testing (PCT) was performed according to PCT-A type method at 90°C with 5 mL of deionized water and 0.25 g of pressed material. The material was removed by drilling into the hard sample surface and crushing the recovered solid with a mortar and pestle. The testing was conducted for 7 days; then the pH of the leachate was measured, the solids were removed from the leachate by 0.45 μm filter, and the leachate was analyzed for Al, Si, Ag, and I concentrations by inductively coupled plasma mass spectrometry (ICP-MS).

3. PHASE IIA and PHASE IIB TESTING

Two phases of testing were conducted in FY 2014. The results from Phase I are summarized in Bruffey et al. (2014), as well as scanning electron microscopy-electron dispersive spectroscopy (SEM-EDS) and XRD results for Phase IIA testing. PCT for Phase IIA and revised density measurements (designated Phase IIB) were completed in FY 2015 and the results are discussed here.

The sample matrix designed for Phase IIA (Table 3) focused on investigating the use of two zeolite materials (sodium zeolite powder and the engineered silver mordenite) and two forms of iodine (sodium iodide and silver iodide).

Table 3: Phase IIA test matrix

Sample[a]	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[a]	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

Table 3: Phase IIA test matrix

Sample[a]	Temperature (°C)	Pressure (MPa)	Particle form and volume ratio	Notes
2-12	900	175	Ground Ag^0Z + AgI (3:1)	Engineered Zeolite
2-13	900	175	Ground Ag^0Z + AgI (6:1)	Engineered Zeolite
2-21	1100	175	NaZ Powder + AgI (3:1)	Pure Zeolite
2-23[a]	900	175	NaZ Powder + NaI (3:1)	Pure Zeolite
2-24	900	175	NaZ Powder + NaI (6:1)	Pure Zeolite

[a]Pressing failure

3.1 Phase IIA: Product Consistency Testing

PCT was conducted on the successfully pressed Phase IIA samples, and the results from the analysis of the leachate are shown in Table 4. Sample 2-7 was found to have released substantially more of each element measured than other samples; it is recommended that this sample be replicated to confirm these results.

Out of the 12 samples tested, six had no measureable release of iodine. From Samples 2-1, 2-2, and 2-3 it can be seen that the amount of iodine leached from the material decreased substantially as pressing temperature was increased from 525°C to 900°C. Sodium release from these samples also followed this trend. Further increase of the pressing temperature to 1100°C for the same sample composition (Sample 2-21) did not result in measurable improvement in leach rate (leached iodine remained below the reporting limit of 1 mg/L, and leached silver rose to slightly above the reporting limit of 5 μg/L)

Samples 2-11 and 2-21, both composed of NaZ powder and AgI (3:1), were pressed at 900°C/100 MPa and 1100°C/175 MPa, respectively. No measurable improvement in leach rate was observed for the higher temperature and pressure used for Sample 2-21. This result combined with the data from Samples 2-1, 2-2, and 2-3 indicate that the majority of the benefit arising from increased temperature may be realized at 900°C and that further elevation may not result in a more durable waste form.

Table 4: Characterization of leachate from PCT testing

Sample	Pressing Conditions T(°C)/P(MPa)	pH of leachate	Na (mg/g)	Al (mg/g)	Si (mg/g)	Ag (μg/L)	I (mg/L)
2-1	525/175	6.18	0.304	ND	0.025	ND	77.0
2-2	700/175	7.78	0.182	0.0084	0.024	5.3	4.1
2-3	900/175	7.22	0.096	ND	0.093	ND	ND
2-5	900/175	7.75	0.174	ND	0.499	11.0	ND
2-6	700/300	7.68	0.218	0.0094	0.282	ND	9.2
2-7	700/300	9.12	0.962	0.0593	1.100	8.0	130.0
2-11	900/100	7.32	0.080	ND	0.032	ND	ND
2-12	900/175	7.99	0.106	0.0290	0.241	5.7	ND
2-13	900/175	7.99	0.098	0.0212	0.245	ND	ND
2-21	1100/175	7.40	0.143	ND	0.179	5.4	ND
2-24	900/175	6.93	0.219	ND	0.054	ND	37.0

ND: Indicates a value below the reporting limit

3.2 Phase IIB (Revised Density Measurements)

Previous density measurements were collected by a simple volume displacement measurement in a graduated cylinder. However, since the samples in the Phase IIA tests resulted in significantly greater compaction of the capsule than expected, the uncertainty in the measure was relatively large. In addition there was some doubt regarding the integrity of several of the initial Phase IIA capsules when void space was observed between the pressed material and the capsule wall. To provide more accurate results, the majority of Phase IIA samples were replicated (and designated as Phase IIB) and the density measured by pycnometer. Ten samples were prepared for pressing, but five of those samples were found to have suffered a significant capsule failure of some type. These failures were manifested by post pressing capsule swelling or failure to compact. The densities of the pressed samples are shown in Table 5. Capsule failure will be discussed in more detail in Section 5. Samples 2-1B, 2-5B, and 2-7B show a significant increase in density upon pressing; this is not observed for samples 2-2B and 2-3B. The lack of increased density for Samples 2-2 and 2-3 may indicate a less obvious capsule failure. There are no clear correlations between density and pressing conditions for these five samples.

Table 5: Density of Phase II-B samples

Sample	Temperature (°C)	Pressure (MPa)	Particle form	Density (g/cc)
2-1B	525	175	NaZ Powder + AgI (3:1)	2.484
2-2B	700	175	NaZ Powder + AgI (3:1)	1.345
2-3B	900	175	NaZ Powder + AgI (3:1)	1.264
2-4B[a]	700	175	NaZ Powder + AgI (6:1)	0.367
2-5B	900	175	NaZ Powder + AgI (6:1)	2.014
2-6B[a]	700	175	NaZ Powder + AgI (6:1)	0.525
2-7B	700	300	NaZ Powder + AgI (3:1)	2.167
2-21B[a]	1100	175	NaZ Powder + AgI (3:1)	0.527
2-23B[a]	900	175	NaZ Powder + NaI (3:1)	0.712
2-24B[a]	900	175	NaZ Powder + NaI (6:1)	1.023

[a]Obvious capsule failure during pressing

4. PHASE IIC TESTING

The sample matrix designed for Phase IIC (Table 6) focused on investigating the use of silver mordenite powder in both pure and engineered forms, with iodine introduced as AgI or by prior chemisorption onto the zeolite.

Table 4: Phase IIC Test Matrix

Sample ID	Temperature (°C)	Pressure (MPa)	Time (h)	Particle form	Notes
2-8	900	175	3	AgZ Powder + AgI (3:1)	Pure Zeolite
2-9	900	175	3	AgZ Powder + AgI (6:1)	Pure Zeolite
2-10	1100	175	3	AgZ Powder + AgI (6:1)	Pure Zeolite
2-14	900	175	3	Ground Ag^0ZI loaded to 2 wt I	Zeolon 900
2-15	900	175	3	Ground Ag^0ZI fully loaded	Zeolon 900
2-16	900	175	3	Ground AgZ fully loaded with I	Zeolon 900
2-17	900	175	3	Ground Ag^0ZI fully loaded + NaZ powder (1:2)	Zeolon 900
2-22	1100	175	3	AgZ Powder + AgI (3:1)	Pure Zeolite

Out of eight prepared samples, four were successfully pressed, and cross-sections of those are shown in Figures 2-5.

Figure 2: Sample 2-8.

Figure 3: Sample 2-9.

Figure 4: Sample 2-16.

Figure 5: Sample 2-17.

Density was measured by pycnometer, and the results are shown in Table 7.

Table 5: Density of Phase IIC Samples

Sample	Temperature (°C)	Pressure (MPa)	Particle form	Density (g/cc)
2-8	900	175	AgZ Powder + AgI (3:1)	3.118
2-9	900	175	AgZ Powder + AgI (6:1)	2.710
2-10[a]	1100	175	AgZ Powder + AgI (6:1)	0.613
2-14[a]	900	175	Ground Ag^0ZI loaded to 2 wt% I	1.206
2-15[a]	900	175	Ground Ag^0ZI fully loaded	0.351
2-16	900	175	Ground AgZ fully loaded with I	2.402
2-17[b]	900	175	Ground Ag^0ZI fully loaded + NaZ powder (1:2)	1.548
2-22[a]	1100	175	AgZ Powder + AgI (3:1)	0.530

[a]Pressing failure
[b]Void space observed in capsule

XRD was performed for Samples 2-8, 2-9, 2-16, and 2-17. The primary phases identified for each sample include Ag, AgI (as iodargyrite), and SiO_2 (as quartz). A representative XRD pattern is shown in Figure 6. The sample composition prior to pressing (pure AgZ vs. engineered AgZ; AgI vs. chemisorbed I) does not correlate to any structural features after sample pressing.

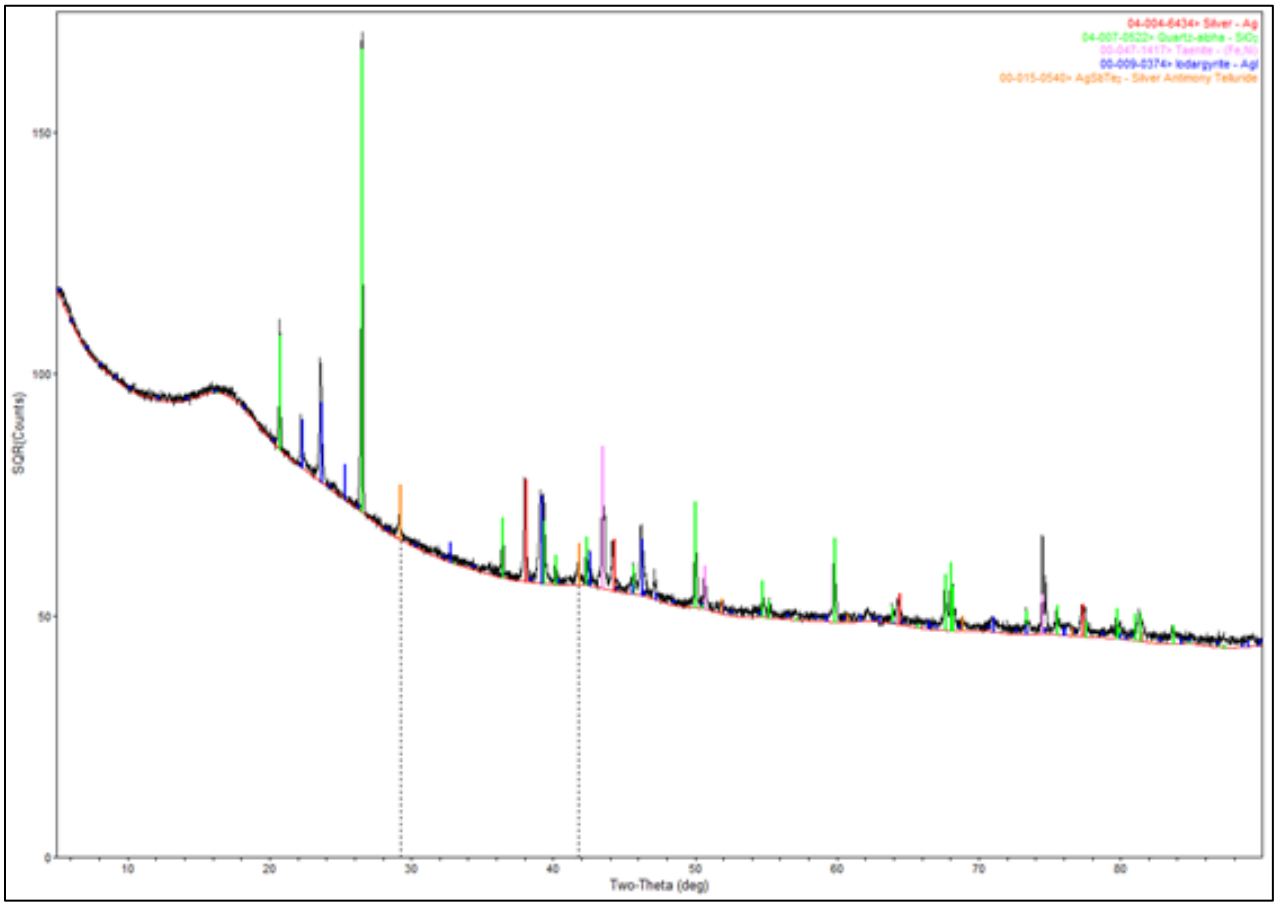

Figure 6: XRD pattern for Sample 2-9 (blue: iodargyrite; green: quartz; red: silver; pink: iron from capsule).

5. PRESSING FAILURES

Phase IIA and IIB of this study were hampered by capsule failures that occurred during pressing throughout FY 2015. In some cases, the failure was immediately obvious upon receipt of the pressed samples from the vendor and appeared to be mechanical. Capsules with mechanical failures generally failed to compress, and in some cases they expanded.

Other failures were not apparent until the capsule was cut open. In some cases, the material was not pressed into a solid monolith and was crumbly or even still powdery in appearance. In other cases, the void space of the interior of the capsule was significant (Figure 7). While significant void space is not technically a pressing failure, it may impact density measurements of the resulting solids.

The source of these failures could be three-fold: (1) welding issues, (2) generation of water vapor in the sample during pressing, and (3) density change from the packed powder to final form was too large and led to excessive capsule deformation. The capsules are prepared by electron beam welding, and the top end cap is sealed on after sample material is loaded into the capsule. As the end caps are very thin (0.010 in.) their connection to the capsule by welding is a difficult operation; it is very easy to burn through the caps or to have miniscule holes within the weld. It is believed that the end cap welding operation (for both top and bottom end caps) may be the source of mechanical failures.

As shown in Eq. (1-4), there can be release of water during the transition between mineral phases. Additionally, mordenite can retain up to 10 wt% water at room temperature. It is speculated that the smaller void spaces in some samples (such as the pitting seen in Figure 2 for Sample 2-8) may be caused

by release of these two sources of water at the high temperatures and pressures of HIP. It is also possible that this same release is preventing formation of a monolith for the samples observed to be crumbly and powdery after pressing.

Finally, the substantial volume and density change of some samples upon pressing may have resulted in capsule deformation beyond what the stainless steel capsule was able to tolerate. This can be observed when samples are compressed to a volume less than 50% of their original size. This excessive capsule deformation is noted in the hollow "wings" in Figures 5 and 7. It is also observed that 75% of samples to date that have been pressed at the temperature extreme of 1100°C did suffer capsule failures. This temperature may be contributing to stress and resultant failure of the capsule, and it is recommended that based on these data and results from the PCT that future testing limit HIP temperature to 900°C.

Figure 7: Sample 2-23B.

6. STRUCTURE OF FY16 WORK

The goals of FY 2016 studies will be to conclude the fundamental research into HIP of AgZ through the use of pure materials, transition to the engineered forms of AgZ or other zeolites that correspond to actual sorbent use, and to initiate work into scaling-up of the HIP process.

6.1 Capsule Integrity Improvements

Mitigation of capsule failure and promotion of monolith formation is critical to the success of continued process development. To minimize mechanical failures, the capsule production method has been modified to use thicker end caps (0.020 in.) and a standard weld for the connection of the bottom end cap to the capsule. The standard weld is thicker than the electron beam weld used for sealing of the capsules after sample loading and is less likely to fail. The electron beam weld will still be required for connection of the top end cap to the capsule, as this weld must be done under vacuum to prepare the sample for pressing. After the electron beam weld has fully sealed the capsule, each capsule will be helium leak checked to ensure the integrity of both types of welds. The capsules will also be leak checked upon return from the commercial HIP vendor to ensure that capsule failure did not occur during pressing.

To minimize the formation of water vapor, the sample components will all be dried at 200°C prior to transfer into the capsules. This drying temperature will remove the majority of the surface water associated with zeolite components. Upon transfer into the capsule, they will be stored in a desiccator or under an inert atmosphere until such time as the electron beam welding is performed. To minimize stress

resulting from capsule compression, the samples will be either pre-pressed by hot uniaxial pressing (HUPing) or firmly tamped into the containers to increase material mass and decrease the void space within the capsule prior to pressing.

6.2 Proposed Test Matrix

To continue the fundamental research and development into this process, a fourth set of samples will be prepared, pressed and analyzed. These samples will be prepared and pressed in duplicate. First, samples correlating to the work performed by Sheppard (2006) that resulted in the formation of sodalite will be created to demonstrate a baseline production method. Second, samples of AgZ either occluded with or containing chemisorbed iodine will be processed according to similar pressing conditions. Finally, the use of alumina as an additive to promote sodalite formation will be investigated. The results from these samples and from earlier work will be used to further refine the envelope of pressing conditions for engineered silver mordenite or other silver zeolites as research moves toward scaling up of sample size. This sample set is briefly detailed in Table 8, with additional parameters such as pressing time, preparation details, and specific sample composition to be determined as sample preparation progresses.

Table 6: Proposed Test Matrix for FY 2016

Sample	Test Objective	Sample composition	HIP conditions T(°C)/P(MPa)
3-1	Baseline	Zeolite A, occluded with AgI	900/190
3-2		Zeolite Y, occluded with AgI	900/190
3-3		Zeolite A, occluded with AgI	900/175
3-4	Optimization of Sample Preparation	NaZ, occluded with AgI	900/175
3-5		NaZ, occluded with AgI	900/300
3-6		Pure AgZ occluded with I or AgI	900/175
3-7		Pure AgZ occluded with I or AgI	900/300
3-8		Chemisorbed I on AgA	900/175
3-9		Chemisorbed I on AgA	900/300
3-10		Chemisorbed on AgZ	900/175
3-11		Chemisorbed on AgZ	900/300
3-12	Improve sodalite formation	AgA, chemisorbed with I, add alumina	900/300
3-13		AgZ, chemisorbed with I, add alumina	900/300

7. CONCLUSIONS

The purpose of this study was to continue research to determine if HIPping could directly convert I-Ag^0Z into a suitable waste form. Research to date has been conducted in three phases.

FY 2015 work completed studies of Phase IIA, IIB, and IIC samples. PCT of Phase IIA samples resulted in iodine release below detection limit for six of twelve samples. This is promising and indicates that a durable waste form may be produced through HIPping even if transformation of the zeolite to a distinct mineral phase does not occur. From PCT results it was determined that future pressing should be conducted at a temperature of 900°C.

Phase IIC testing continued production of samples to examine the effects of multiple source materials, compositional variations, and an expanded temperature range. The density of each sample was determined, and XRD patterns were obtained. In all cases, there was nothing in the XRD analyses to indicate the creation of any AgI-containing silicon phase; the samples were found to be largely amorphous.

Progress was impaired due to multiple capsule failures throughout the year. Mitigation of capsule failures will be a critical component to the success of continued work. Additionally, there is concern that PCT is not suitable for the determination of long-term stability of heterogeneous waste forms such as those that are produced by HIP. Other testing methods will be considered and initiated in collaboration with waste form experts. The ultimate goal of investigations into HIPping of Ag^0Z-I is to produce a pellet that can be demonstrated to have high iodine retention and be considered to be a promising candidate for long-term stability and disposition of iodine-containing zeolite sorbents.

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8. REFERENCES

Anderson, K. K., et al. *Iodine Loading of Partially Reduced Silver Mordenite*, FCRD-SWF-2013-000079, U.S. Department of Energy Separations and Waste Forms Campaign, 28 December 2012.

Bruffey, S. H., et al. *Expanded Analysis of Hot Isostatic Pressed Iodine-Loaded Silver-Exchanged Mordenite*, FCR&D-SWF-000278, U.S. Department of Energy Separations and Waste Forms Campaign, September 2014.

Fukumoto, M. *Method for Solidifying Waste Containing Radioactive Iodine*, U.S. Patent No. 5826203, 1998.

ICDD, PDF-4+, International Centre for Diffraction Data, Newtown Square, Penn., 2013.

Jade, version 9.4.5 (computer software), Materials Data Inc., Livermore, Calif., 2012.

Jubin, R. T. *Report of the FY11 Activities of the Off-Gas Sigma Team*, FCR&D-SWF-2011-000306, U.S. Department of Energy Separations and Waste Forms Campaign, September 2011.

Jubin, R. T.; and Bruffey, S. H. "Initial Evaluation of a Hot Isostatic Pressed Waste Form from Iodine-Loaded Silver-Exchanged Mordenite." Accepted, *Global 2015, Nuclear Fuel Cycle for a Low Carbon Future.*

Perera, D.; Vance, E. R.; Trautman, R.; and Begg, B. "Current Research on I-129 Immobilization," In *Proceedings of WM'04*, Waste Management, Tucson, Ariz., 2004.

Sheppard, G. P.; Hriljac, J. A.; Maddrell, E. R.; and Hyatt, N. C. "Silver Zeolites: Iodide Occlusion and Conversion to Sodalite—A Potential I-129 Waste Form?" In *Scientific Basis for Nuclear Waste*

Management XXIX, ed. P Van Iseghem, Vol. 932, pp. 775–82. Materials Research Society, Warrendale, Pennsylvania, 2006.

Strachan, D. M. and Babad, H. *Iodide and Iodate Sodalites for the Long-Term Storage of Iodine-129*, Report No. RHO-SA-83, Rockwell Hanford Operations, Richland, Wash., 1979.