Preparation of Four Large-Format Hot Isostatically Pressed I–AgZ Waste Form Samples for Performance Testing

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SUMMARY

Hot isostatic pressing (HIP) is being considered as a process to directly convert ^{129}I-bearing materials to a durable radiological waste form. Zeolites, specifically silver-exchanged mordenite (AgZ), have been studied extensively as potential radioactive iodine sorbents and will contain ^{129}I as chemisorbed AgI, a relatively insoluble compound with a high melting point. Oak Ridge National Laboratory has conducted several recent studies on the HIP of both I–AgZ and other iodine-bearing zeolites, resulting in an inventory of samples prepared with a suite of zeolites with varied iodine incorporation methods, pressing conditions, and sizes. These samples have been made available to researchers at other national laboratories in support of test method development to assess the stability of heterogenous iodine-bearing waste forms. The work described here generated four large-format HIPed I–AgZ samples. These samples are 1.5 in. diameter and 2 in. length and contain 49 g of I–AgZ. Two samples were prepared at an iodine loading of 64 mg I/g I–AgZ, and two samples were prepared at an iodine loading of 135 mg I/g I–AgZ. These two sets of duplicate samples will be made available upon request in support of iodine waste form durability method development efforts.

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ACRONYMS

AgZ	silver-exchanged mordenite
Ag^0Z	hydrogen-reduced silver-exchanged mordenite
FY	fiscal year
I-AgZ	iodine-loaded AgZ
HIP	hot isostatic pressing
NAA	neutron activation analysis
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory

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PREPARATION OF FOUR LARGE-FORMAT HOT ISOSTATICALLY PRESSED I–AGZ WASTE FORM SAMPLES FOR PERFORMANCE TESTING

1. INTRODUCTION

Hot isostatic pressing (HIP) is being considered as a process for direct conversion of ^{129}I-bearing materials to a durable radiological waste form. The removal of volatile radioactive ^{129}I from the off-gas of a nuclear fuel reprocessing facility will be necessary to comply with regulatory requirements regarding reprocessing facilities sited within the United States, and any iodine-containing media or solid sorbents generated by off-gas abatement processes will require disposal (Jubin et al. 2012). Zeolites, specifically silver-exchanged mordenite (AgZ), have been studied extensively as potential radioactive iodine sorbents and will contain ^{129}I as chemisorbed AgI, a relatively insoluble compound with a high melting point. Oak Ridge National Laboratory (ORNL) has conducted several recent studies on the HIP of both I–AgZ and other iodine-bearing zeolites. These studies have resulted in an inventory of samples prepared with a suite of zeolites with varied iodine incorporation methods, pressing conditions, and sizes (Bruffey et al. 2015, 2016a, 2016b, 2017a, 2017b). These samples have been made available to researchers at other national laboratories to support test method development to assess the stability of heterogenous iodine-bearing waste forms (Asmussen et al. 2018; Ebert et al. 2017). The work described here generated four large-format HIPed I–AgZ samples that are intended to be used in these method development efforts.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Preparation of I–AgZ

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16). It contains 11.9 wt% silver and has a 0.16 cm pellet diameter. Before use in testing, the sorbent material was reduced by exposure to a 4% H_2 blend in argon at 270°C for 10 days. After reduction, the material was stored under argon to limit oxidation by air. Details of this procedure are provided by Anderson et al. (2012).

To provide homogeneously loaded I–AgZ, a large thin bed system was fabricated that allowed a one to two pellet deep layer of hydrogen reduced AgZ (Ag^0Z) to be saturated with iodine in a closed tube at elevated temperature. The Ag^0Z was supported on an 18 in. length of metal mesh screen (Figure 1). This screen was placed in a 6 in. diameter glass pipe (procured from Ace Glass), and iodine was distributed onto the bottom of the glass pipe (Figure 1). The pipe was sealed using glass end caps and high-temperature gaskets from Ace Glass. Two batches of I–AgZ were prepared. The first (AgZ-10) was prepared with the intent of saturating the material (i.e., completely reacting all silver in the material with iodine to form AgI). The second (AgZ-5) was prepared with the intent of reacting roughly 33% of the silver contained in the material with iodine to form AgI. Roughly stoichiometric amounts of iodine (assuming a 1:1 ratio of Ag:I in the loaded sorbent) were placed in the pipe to achieve the target iodine loadings. For sample AgZ-10 15.53 g of iodine was used; for sample AgZ-5 5.24 g of iodine was used.

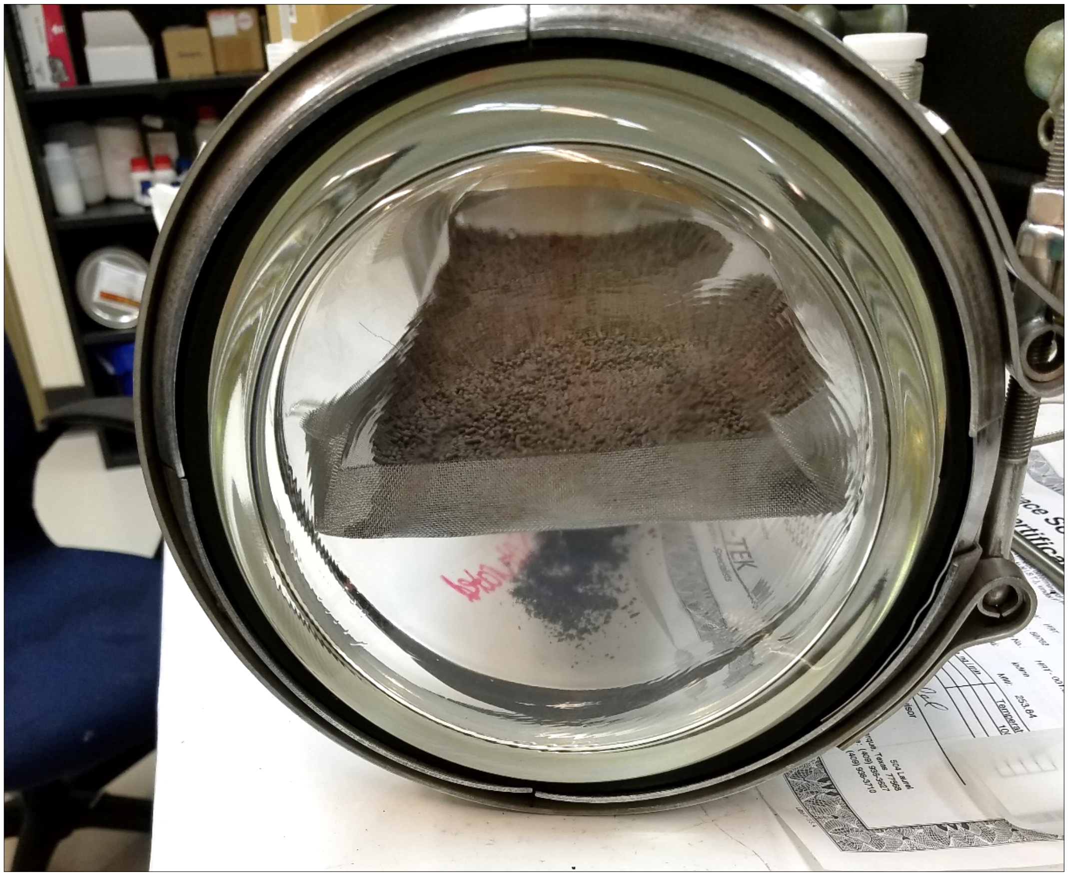

Figure 1: Sealed glass pipe used for AgZ loading (end view).

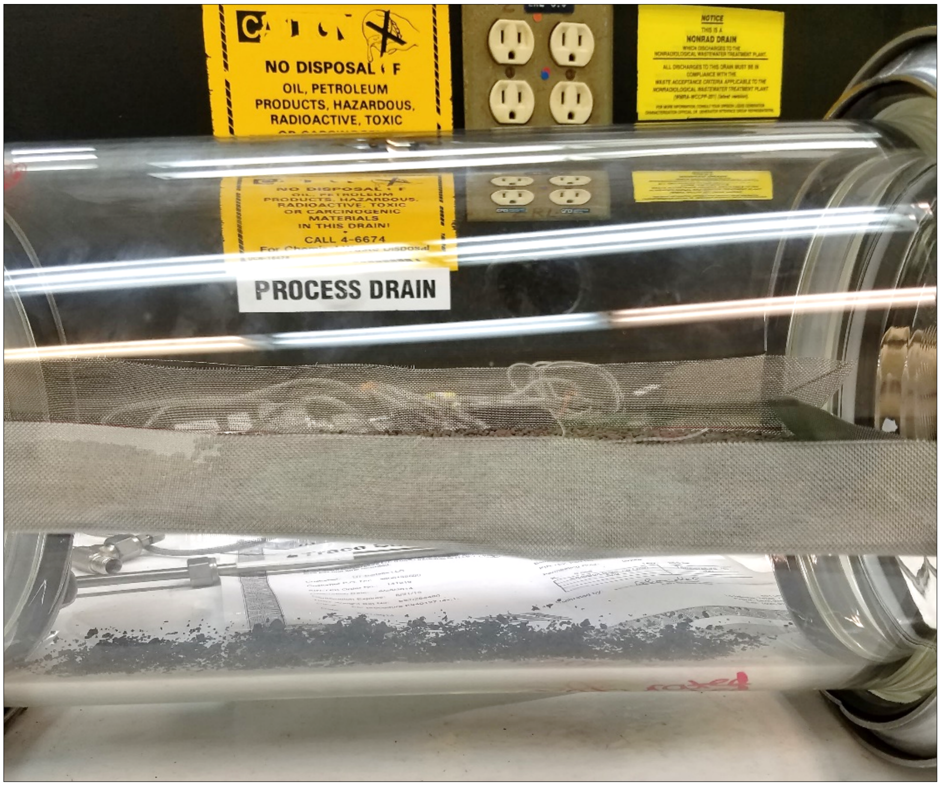

Figure 2: Sealed glass pipe used for AgZ loading (side view).

The sealed glass pipes were placed in an oven and held at 150°C for 11 days. No iodine solids were observed upon removal of the pipes from the oven. AgZ-10 was observed to be light brown, and AgZ-5 was observed to be light green (Figure 3). Weight measurements of the samples after contact showed weight increases of 16.24 g for AgZ-10 and 6.39 g for AgZ-5 (Table 1). Some of the observed weight gain may be due to water adsorption during handling in room air.

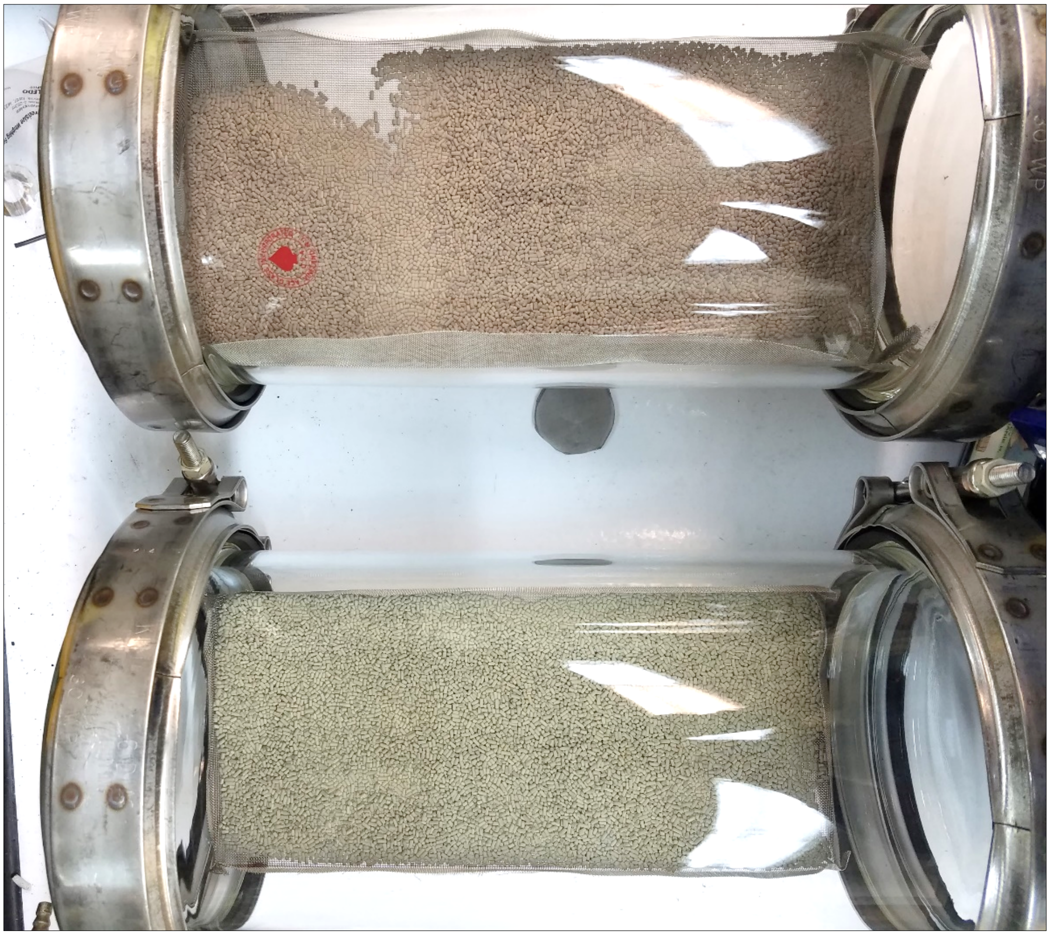

Figure 3: Top view: AgZ following removal from the oven (Top: AgZ-10, Bottom: AgZ-5).

After removal from the oven, both materials were purged by placing each in separate glass columns and flowing with dry air (less than −65°C dew point) at 1 LPM for 2 days in an oven held at 150°C. Air purge of AgZ-5 resulted in a loss of 7.7% of the weight gained during the thin-bed loading. The amount of weight lost during the dry-air purge was not able to be determined for AgZ-10 as several pellets were lost during recovery from the column used to contain the material during purging. The materials were analyzed by neutron activation analysis (NAA) at ORNL's High Flux Isotope Reactor to determine iodine content, and this number is shown in Table 1. This iodine loading is calculated using the iodine-loaded sorbent weight. The NAA analysis was performed in duplicate, and the range of results received is shown. The iodine content reported for AgZ-5 varied from 55.5 to 73.8 mg/g I-AgZ, and archived samples will be analyzed to improve the fidelity of this value. Both results for AgZ-5 indicate that the sorbent contains more iodine than was loaded into the system, and so this number should be considered preliminary until confirmed by further analysis. In the case of AgZ-10, the iodine retained by the sorbent represents a silver utilization of 97%.

Table 1: Observed and final sorbent weight gain

Material	Initial Weight (g)	Iodine used (g)	Weight after contact (g)	Weight gained during contact (g)	Weight after air purge (g)	Final iodine loading [B] (mg/g I-AgZ)	Iodine absorbed by sorbent [B] (g)
AgZ-10	100.45	15.53	116.69	16.24	*Not measured* [A]	134.3–135.8	15.54–15.74
AgZ-5	100.19	5.24	106.58	6.39	106.09	55.5–73.8	5.89–7.98
[A] *During removal of the material from the column used for dry-air purge, several pellets were lost.*							
[B] *As measured by neutron activation analysis*							

2.2 Capsule Loading and Sealing

The materials were placed into 304 stainless steel capsules. These capsules were 1.5 in. diameter and 2 in. length with a wall thickness of 0.02 in. These capsules were sized identically to previously prepared large-format samples. The lid is an inset trepan lid with a vent port to aid in capsule sealing. The wall thickness of the tubing and the end cap was 0.020 in. The material was poured into the capsule and tapped gently on the benchtop to pack the material into each capsule. The loaded capsules are shown in Figure 4. Each capsule contains 49 g of I–AgZ.

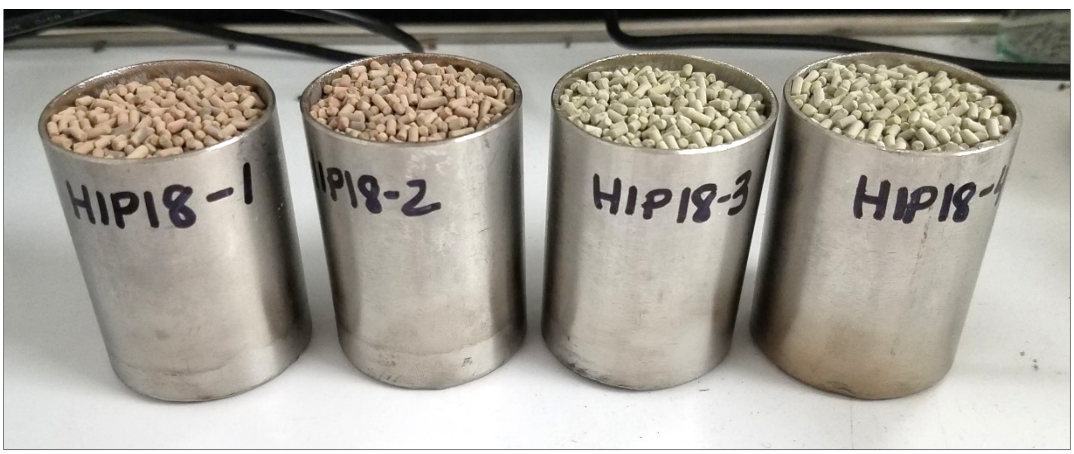

Figure 4: I–AgZ in stainless steel capsules before sealing.

The lid of each sample was welded onto the capsule on a benchtop and transferred to a vacuum box for closure of the vent port by electron beam welding. Each sample was hydrostatically leak-checked after sealing, and no leaks were identified up to pressures of 1,450 PSI. The sealed capsules are shown in Figure 5.

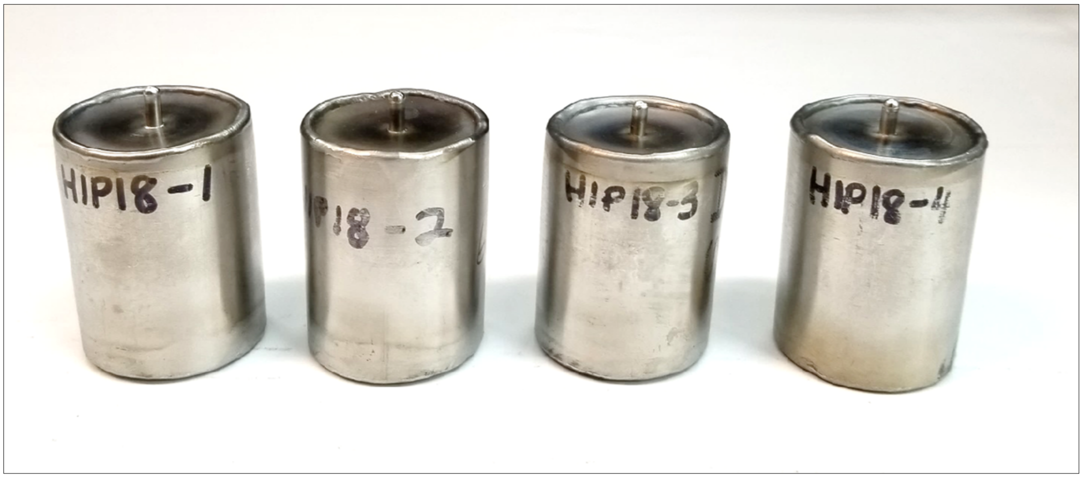

Figure 5: Sealed capsules.

2.3 Hot Isostatic Pressing of Capsules

The samples were processed using HIP by American Isostatic Presses Inc. at 900°C and 300 MPa with a 3-hour hold time. The pressed samples are shown in Figure 6.

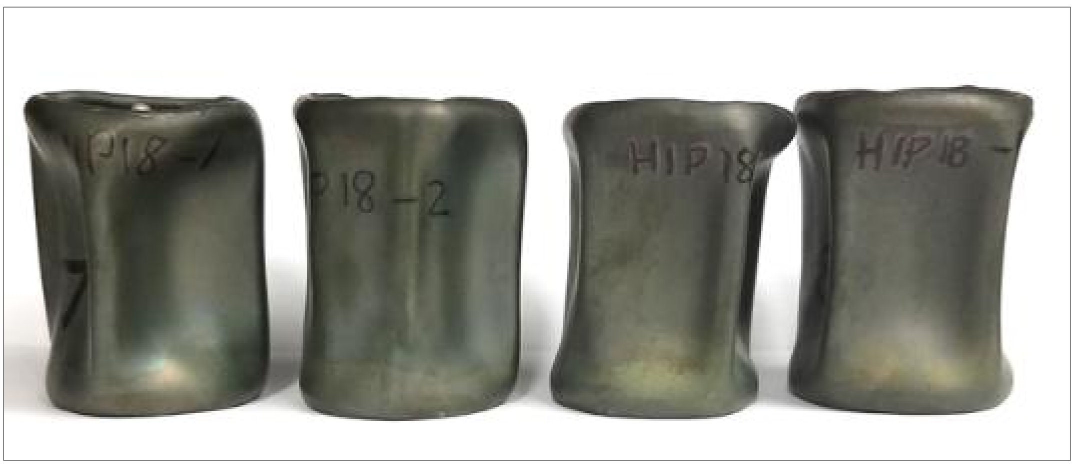

Figure 6: Pressed capsules

3. CONCLUSIONS

Samples prepared at ORNL to support the conversion of I–AgZ to a durable waste form using HIP are available to researchers as requested to support waste form durability test method development. The samples prepared at ORNL over the past 2 years are listed in Appendix A, and the samples associated with this specific effort are highlighted in gray. Samples generated in fiscal years (FYs) 2015 and 2016 are detailed in Bruffey et al. 2017a.

4. REFERENCES

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Appendix A

Samples Prepared at ORNL in Fiscal Years 2017 and 2018

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A-1. Samples Prepared at ORNL in Fiscal Years 2017 and 2018

Sample	Temp. (°C)	Pressure (MPa)	Time (h)	Iodine content mg/g I–AgZ	Drying temp. (°C)	Characterization performed?	Notes
HIP17-1	700	100	3	88	None	Yes	
HIP17-2	700	175	3	88	None	Yes	Transferred to Pacific Northwest National Laboratory (PNNL) fiscal year (FY) 2018
HIP17-3	700	175	3	88	None	Yes	
HIP17-4	700	175	3	88	None	Yes	
HIP17-5	700	300	3	88	None	Yes	
HIP17-6	900	100	3	88	None	Yes	Transferred to PNNL FY 2018
HIP17-7	900	175	3	88	None	Yes	
HIP17-8	900	175	3	88	None	Yes	Transferred to PNNL FY 2018
HIP17-9	900	175	3	88	None	Yes	
HIP17-10	900	300	3	88	None	Yes	
HIP17-11	1100	100	3	88	None	Yes	
HIP17-12	1100	175	3	88	None	Yes	
HIP17-13	1100	175	3	88	None	Yes	
HIP17-14	1100	175	3	88	None	Yes	
HIP17-15	1100	300	3	88	None	Yes	
HIP17-16	900	175	6	88	None	Yes	
HIP17-17	900	175	12	88	None	Yes	Transferred to PNNL FY 2018
HIP17-18	525	100	3	88	None	Yes	Transferred to PNNL FY 2018
HIP17-19	525	100	12	88	None	Yes	
HIP17-20	900	175	3	88	150	Yes	

<table>
<tr><th>Sample</th><th>Temp. (°C)</th><th>Pressure (MPa)</th><th>Time (h)</th><th>Iodine content mg/g I–AgZ</th><th>Drying temp. (°C)</th><th>Characterization performed?</th><th>Notes</th></tr>
<tr><td>HIP17-21</td><td>900</td><td>175</td><td>3</td><td>88</td><td>270</td><td>Yes</td><td></td></tr>
<tr><td>HIP17-22</td><td>900</td><td>175</td><td>3</td><td>88</td><td>450</td><td>Yes</td><td>Transferred to PNNL FY 2018</td></tr>
<tr><td>HIP17-23</td><td>900</td><td>175</td><td>3</td><td>88</td><td>450</td><td>Yes</td><td></td></tr>
<tr><td>HIP17-24</td><td>900</td><td>175</td><td>3</td><td>88</td><td>450</td><td>No</td><td>Failed capsule</td></tr>
<tr><td>HIP17-25</td><td>900</td><td>300</td><td>3</td><td>54</td><td>None</td><td>No</td><td>AgI powder</td></tr>
<tr><td>HIP17-26</td><td>900</td><td>175</td><td>3</td><td rowspan="3">100 (estimated)</td><td>None</td><td>Yes</td><td>Large-format sample</td></tr>
<tr><td>HIP17-27</td><td>900</td><td>175</td><td>3</td><td>None</td><td>Yes</td><td>Large-format sample</td></tr>
<tr><td>HIP17-28</td><td>900</td><td>175</td><td>3</td><td>None</td><td>Yes</td><td>Large-format sample</td></tr>
<tr><td>HIP17-29</td><td>900</td><td>100</td><td>3</td><td>21</td><td>None</td><td>Yes</td><td></td></tr>
<tr><td>HIP17-30</td><td>900</td><td>175</td><td>3</td><td>22</td><td>None</td><td>No</td><td></td></tr>
<tr><td>HIP17-31</td><td>900</td><td>300</td><td>3</td><td>30</td><td>None</td><td>No</td><td></td></tr>
<tr><td>HIP18-1</td><td>900</td><td>300</td><td>3</td><td>135</td><td>150</td><td>No</td><td rowspan="2">Large-format, replicate samples</td></tr>
<tr><td>HIP18-2</td><td>900</td><td>300</td><td>3</td><td>135</td><td>150</td><td>No</td></tr>
<tr><td>HIP18-3</td><td>900</td><td>300</td><td>3</td><td>64</td><td>150</td><td>No</td><td rowspan="2">Large-format, replicate samples</td></tr>
<tr><td>HIP18-4</td><td>900</td><td>300</td><td>3</td><td>64</td><td>150</td><td>No</td></tr>
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