Quantify the Extent of Physisorption on Silver Based Sorbents under VOG Conditions

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SUMMARY

US regulations govern release limits for volatile radionuclides contained in the gaseous effluents of used nuclear fuel reprocessing facilities. Of the four volatile radionuclides that are most restricted by the release limits (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I), ^{129}I will require the greatest degree of abatement. Within a reprocessing facility, the vessel off-gas stream will likely contain 1%–5% of the total iodine at parts per billion (ppb) concentrations. Studies conducted by the authors have now investigated both I_2 and methyl iodide (CH_3I) adsorption by two silver-bearing sorbents, hydrogen-reduced silver-exchanged mordenite (Ag^0Z) and silver functionalized aerogel (AgAerogel) at a range of concentrations up to 1,000 ppb. Throughout this suite of tests, and particularly in the case of CH_3I adsorption tests, there was a significant discrepancy in the amount of iodine recovered on sorbent beds compared to the amount of iodine that was believed to be delivered to the test system.

This study evaluated the effect that sample removal procedures, specifically vacuum removal, may have on the measured iodine content of the sorbent. If sample removal procedures are biasing the measured iodine content of the loaded sorbent, this could explain the incomplete mass balance observed in previous testing. A total of five tests were conducted in which Ag^0Z was contacted with either an I_2- or CH_3I-bearing humid gas stream ($[I_2]$ = 100 ppb; $[CH_3I]$ = 200 ppb) for a loading duration of 18 days. The sorbent material was sampled using two different methods, and the iodine loadings for each removal method (vacuum and pouring) were compared.

Tests 1–3 were observed to have iodine loadings near or below the detection limit of the analysis. These results led to system adjustments before completion of Tests 4 and 5. Tests 4 and 5 showed quantifiable recoveries of iodine on the sorbent and were used to evaluate the effects of the sample removal method on the measured iodine content of Ag^0Z challenged with CH_3I. Related testing from a separate project was used to provide information about how the sample removal method might affect the measured iodine content of Ag^0Z challenged with I_2.

These duplicate tests showed that no quantifiable amount of adsorbed iodine (fed as CH_3I) was removed by vacuum during sampling when Ag^0Z is not saturated. None of the analyzed bed segments displayed variation in total iodine loading as a result of vacuum retrieval. Previously reported testing also indicated that vacuum removal does not affect adsorbed iodine on Ag^0Z when it is fed as elemental iodine (I_2). These results indicate that the incomplete recovery of iodine on silver-based sorbent beds previously observed by the authors is not an artifact of the sample removal method.

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1. INTRODUCTION

US regulations govern release limits for volatile radionuclides contained in the gaseous effluents of used nuclear fuel reprocessing facilities. Of the four volatile radionuclides that are most restricted by the release limits (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I), ^{129}I will require the greatest degree of abatement (Jubin et al. 2012). Previous studies have shown that overall plant decontamination factors for ^{129}I must, at minimum, exceed 1,000 to meet regulatory requirements. Iodine-containing off-gas will be present in the dissolver off-gas, the cell off-gas, the vessel off-gas (VOG), the waste treatment off-gas, and the shear off-gas. The VOG will most likely contain 1%–5% of the total iodine at parts per billion (ppb) concentrations. A number of studies have examined iodine abatement from the dissolver off-gas, which contains greater than 95% of the iodine inventory of the plant, but until recently, there were few published studies on the abatement of volatile iodine from the VOG stream (Jubin et al. 2013).

Studies conducted by the authors have now investigated both I_2 and methyl iodide (CH_3I) adsorption by two silver-bearing sorbents, hydrogen-reduced silver-exchanged mordenite (Ag^0Z) and silver functionalized aerogel (AgAerogel) at a range of concentrations up to 1,000 ppb (Jubin et al. 2015; Bruffey et al. 2016a, Bruffey et al. 2016b; Jubin et al. 2017; Jubin et al. 2018). Throughout this suite of tests, and particularly in the case of CH_3I adsorption tests, there was a significant discrepancy in the amount of iodine recovered compared to the amount of iodine that was believed to be delivered to the test system. Jubin et al. (2017) recommended that future work in this area focus on resolving these outstanding questions about the closure of the material balance. The study described here investigates the effect that sample retrieval procedures may have on the measured iodine content of the sorbent and the resulting observed mass balance.

1.1 Material Balances Observed in Previous Testing

A summary of the iodine recoveries observed to date by the authors across several experimental efforts is shown in Table 1. Generally, it was observed that iodine recovery on the sorbent was higher with I_2, rather than CH_3I, as the adsorbing species. It was also noted that iodine recovery was greater than >100% in some cases.

Table 1. Iodine recoveries in previously reported testing.

Test ID	Species	Concentration (ppb)	Iodine recovery (%)	Iodine feed system	Reference
Ag^0Z					
2015-VOG2	CH_3I	40	33	Blended gas cylinder	Jubin et al. 2015
2016-VOG-002	I_2	7	84	Certified permeation tubes	Bruffey et al. 2016a
2017-VOG-T4	I_2	500	100	Crystalline I_2 generator	Jubin et al. 2017
2017-VOG-T5(4)	CH_3I	400	39	Certified permeation tubes	
2017-VOG-T7(4)	CH_3I	1,000	50		
2018-ExtVOG	I_2	50	102		Jubin et al. 2018
AgAerogel					
2016-VOG-T3	CH_3I	40	50	Blended gas cylinder	Bruffey et al. 2016b
2016-VOG-T4	I_2	7	165	Certified permeation tubes	
2017 T5-Aerogel	CH_3I	400	114		Jubin et al. 2017
2017 T7-Aerogel	CH_3I	1,000	80		
2017 T4-Aerogel	I_2	500	67	Crystalline I_2 generator	

1.2 Proposed Causation

Three hypotheses were put forth to explain inconsistent iodine recovery on the sorbent test beds. The first suggested that the expected amount of iodine was not being delivered to the sorbent bed because of problems with either iodine feed gas generation or with the test system itself (system gas leaks or iodine consumption by corrosion). A number of system modifications were implemented to minimize potential iodine generation or test system problems, and those are detailed in Section 1.3.

The second proposed hypothesis was that the sorbent beds are <100% efficient in removing organic iodine, with some organic iodine passing through the sorbent beds without being recovered. Direct monitoring of the iodine concentration in the effluent stream could determine whether iodine is passing through the bed, but this measurement is difficult, especially for testing at prototypic VOG conditions where in the effluent iodine concentration could be at parts-per-trillion levels. Additionally, any analytical measurement would have to account for multiple iodine species, as organic iodine has been shown to decompose to I_2 and HI across an Ag^0Z bed (Nenoff et al. 2014).

The third hypothesis presented was that the sample retrieval procedures biased the measured iodine content. To date, the authors have removed the iodine-loaded sorbent from sorbent columns using a light-duty laboratory vacuum pump. If a fraction of iodine in the bed is physisorbed, rather than chemisorbed as expected, it could be removed during this vacuum step. The purpose of the testing described in this report was to investigate this sampling method and its potential effects on measured iodine content. A total of five tests were conducted in which Ag^0Z was contacted with either an I_2- or CH_3I-bearing humid gas stream ($[I_2]$ = 100 ppb; $[CH_3I]$ = 200 ppb) for a loading duration of 18 days. The sorbent material was sampled using two different methods, and the iodine loadings for each removal method were compared.

1.3 System Modifications

As the tests summarized in Table 1 were executed, a number of system modifications were completed with the intention of minimizing iodine loss within the system and improving the fidelity of the methyl iodide feed source. Iodine losses within the system could occur through corrosion of piping and construction materials or through gas leaks within the feed lines or within the sorbent column assembly itself. The CH_3I feed source for early tests (2015–2016) was a gas blend intended to provide 1,000 ppm CH_3I (bal. N_2) to the feed system, where it was then diluted with humid air to the target concentration. This gas blend was contained within a carbon steel cylinder. This cylinder served as a potential iodine loss point (via corrosion) and co-incident testing on other projects indicated that some cylinders were not delivering iodine to the feed system at the concentration expected. In the two tests that that used this CH_3I gas blend, 2015-VOG2 and 2016-VOG-T3, the recoveries of iodine were 33% and 50%, respectively.

The gas cylinders were replaced by a CH_3I feed stream generated by CH_3I permeation tubes contained in a Kin-Tek Flexstream gas generator. Concurrently, the glass test assembly containing the silver sorbent was redesigned to minimize potential leaks from the sorbent column assembly. The test systems are typically composed of several glass columns in series, and the columns were originally connected by ground glass ball and socket joints. These joints were easily misaligned, and the connections were redesigned to instead use Swagelok Ultra-Torr fittings. These fittings are stainless steel with FKM O-rings and have a certified helium leak rate of 4×10^{-9} std cm^3/s at ambient temperature.

Subsequent testing used a Kin-Tek gas generator and a redesigned test assembly, shown in Figure 1. Leak checks were performed on the feed system lines to ensure that the lines were able to hold either a vacuum or a gas at a pressure of 15–20 psig. The test assembly itself cannot be leak checked by positive pressure or vacuum because of the glass construction and use of ground glass joints to connect the base and top of the sorbent columns. The CH_3I tests performed after these modifications showed iodine recoveries of 39%, 50%, 80%, and 114% (2017-VOG-T5[4], 2017-VOG-T7[4], 2017 T7-Aerogel, and 2017 T5-Aerogel, respectively). This iteration of the test system, consisting of a Kin-Tek gas generator and the redesigned test assembly shown in Figure 1, was used for the testing reported here.

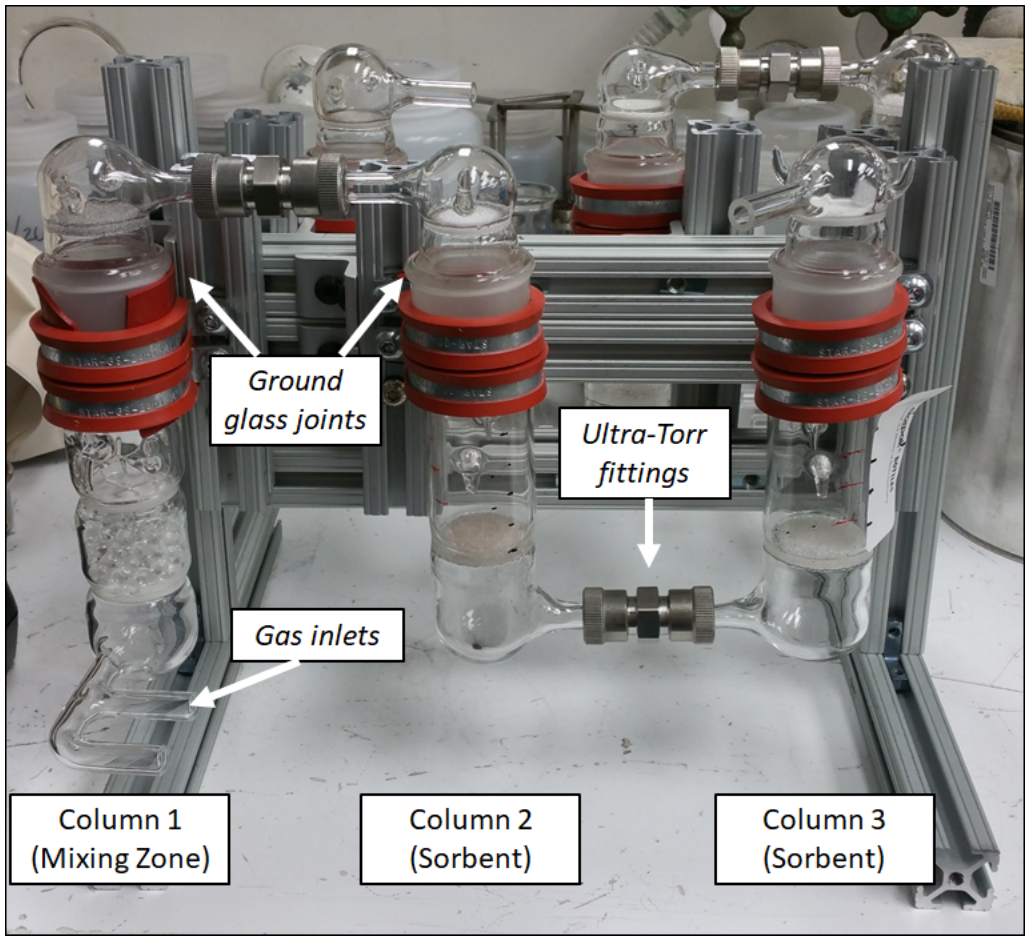

Figure 1. VOG test system using Swagelok Ultra-Torr fittings to connect glass columns in series.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Test System and Materials

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16). It contains 9.5 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 nitrogen 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). The reduced AgZ (Ag^0Z) had a measured bulk density of 0.84 g/cm^3.

To minimize corrosion from iodine-bearing humid air streams, the materials of construction for the system were carefully selected to minimize iodine retention on system components and piping. The sorbent beds were contained within glass columns (internal diameter = 3.45 cm). Three sorbent beds were placed in series. These beds were contained in glass sorbent columns connected by Swagelok Ultra-Torr fittings. For each test, Bed 1 contained ~5 g Ag^0Z, Bed 2 contained ~10 g Ag^0Z, and Bed 3 contained ~ 5 g Ag^0Z. A schematic of the test system is shown in Figure 2.

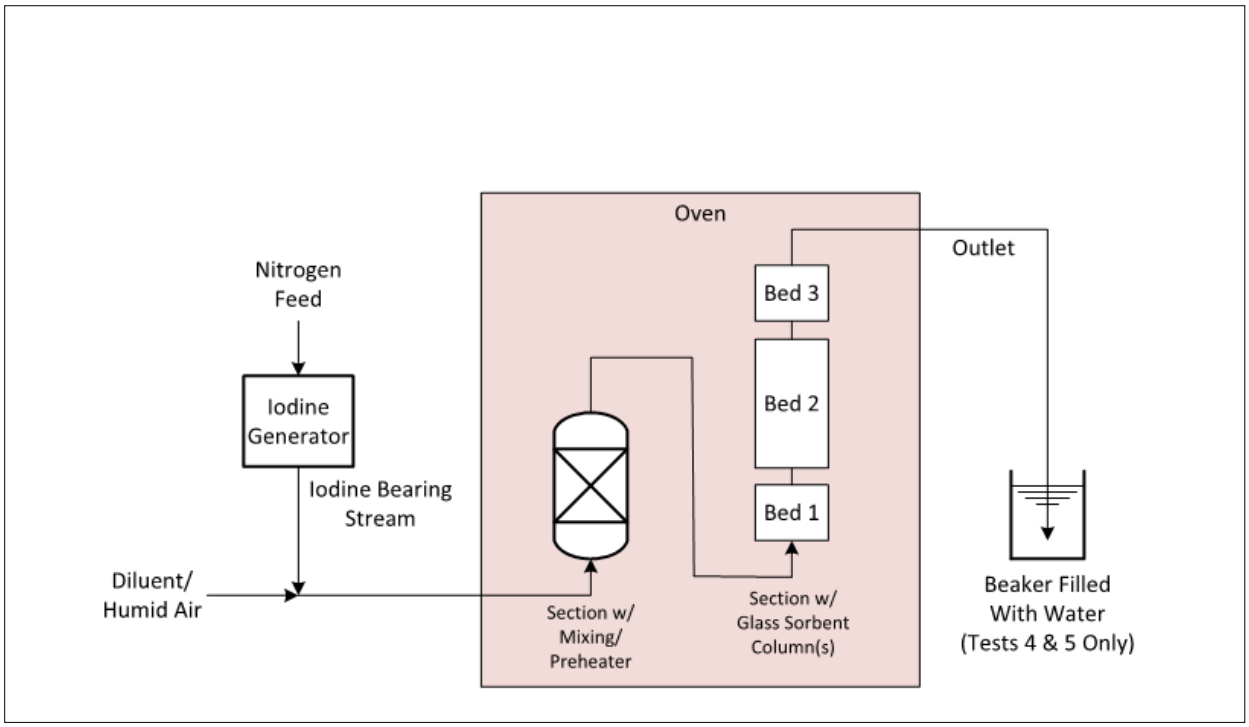

Figure 2. Schematic of VOG test system.

Gas streams were generated using permeation tubes provided by Kin-Tek Analytical and contained within a Kin-Tek Flexstream gas generator. Nitrogen was passed through a glass chamber containing permeation tubes that released CH_3I or I_2 at a predetermined rate at a specified temperature. This was then fed to the process and diluted with the humid air stream. The permeation tubes were certified by gravimetric analysis by the manufacturer before delivery; delivery rates were known to within 1 ng/min. The permeation tubes used in this testing had an emission rate of ~6,000 ng/min at 50°C for CH_3I. Three permeation tubes were contained in a single Kin-Tek unit to generate I_2-bearing gas streams at the desired concentration. Elemental iodine permeation tubes were certified to have an emission rate of ~2,000 ng/min at 100°C. The total gas flow rate, including the iodine-bearing stream, dilution stream, and humidified air stream, was 6.3 LPM.

The humid air and CH_3I or I_2 supply stream were piped through separate lines of tubing until they were blended together at high temperature (150°C) in a mixing zone before introduction into the sorbent bed. This mixing zone consisted of glass beads (diameter ~3 mm) contained in a glass column with the same diameter as the sorbent columns. The system was visually examined for signs of corrosion before testing. Leak checks were performed on the feed system lines to ensure that the lines were able to hold a vacuum of 15–20 psig pressure. Table 2 summarizes completed testing.

Table 2. Test descriptions.

Test	Iodine form and nominal concentration	Emission rate of permeation tubes (ng/min)	Ag^0Z used (g)			
			Bed 1	Bed 2	Bed 3	Total
1	CH_3I; 200 ppbv	6087	5.0970	9.8880	5.0740	20.0590
2	I_2; 100 ppbv	2203, 2084, 2065	5.0399	10.0615	5.0229	20.1243
3	I_2; 100 ppbv		5.2233	10.0728	5.1151	20.4112
4	CH_3I; 200 ppbv	6054	5.2275	10.2251	5.1817	20.6343
5	CH_3I; 200 ppbv	6112	5.5117	9.9910	5.4283	20.9310
Note: Tests 4 and 5 were conducted at replicate test conditions.						

2.2 Sampling and Analysis

Sampling was performed similarly for each test. Each bed segment was gently poured out of the column and subsampled three to five times. The portion of the bed that remained after subsampling was returned to the column, vacuumed out, and subsampled again. This method allowed for any differences between the poured and vacuumed segments to be attributed to the removal of iodine by the vacuum, rather than by differences between tests or variation within beds. Selected subsamples were analyzed by neutron activation analysis at Oak Ridge National Laboratory's High Flux Isotope Reactor to determine iodine content, reported as mg I/g loaded sorbent (mg I/g I-Ag^0Z). Samples not analyzed were archived to be analyzed in the future as needed.

The 95% confidence limit for the iodine content of samples and the amount of iodine recovered by the sorbent beds was calculated using the Student t-distribution, chosen because of the small sample size of each bed(two to three replicates per removal method with a total of five to six samples per bed).

3. RESULTS

The amount of iodine recovered by the sorbent beds is shown in Table 3. The first three tests were observed to have iodine loadings near or below the detection limit of the analysis. These results led to additional system adjustments that are described in Section 3.1. Tests 4 and 5 showed quantifiable recoveries of iodine on the sorbent and were used to evaluate the effects of sample removal method on the measured iodine content of Ag^0Z challenged with CH_3I (Section 3.2) As Tests 1–3 did not show quantifiable of amounts iodine on the sorbent beds, related testing from a separate project was used to provide information about how the sample removal method might affect the measured iodine content of Ag^0Z challenged with I_2 (Section 3.3).

Table 3. Iodine recovery on sorbent beds.

Test	Iodine form	Iodine recovered on sorbent beds (%)
1	CH_3I	1[a]
2	I_2	0[a]
3	I_2	2[a]
4	CH_3I	31.1 ± 14.5[b]
5	CH_3I	98.2 ± 3.3[b]

[a] Error in recovery not calculated; iodine loadings of sorbent were near or below detection limit.
[b] The 95% confidence limit was based on the average of all samples in each sorbent bed (no binning for removal method).

3.1 System Adjustments based on Tests 1–3 Results

Analysis of sorbents recovered from Tests 1–3 showed very low levels of iodine loading on every bed. Receipt of these results prompted evaluation of the test system. The system was visually inspected for corrosion, and the system was assessed for any remaining leak points that were not resolved in previous system modifications (discussed in Section 1.3). As shown in Figure 1, there are ground glass joints connecting the column body and column head. It was determined that these ground glass joints could become unseated during test start up, causing a gross leak of the feed gas stream before its contact with the sorbent beds. A water-filled beaker was placed on the effluent line during Tests 4 and 5 to provide visual verification of flow. This is a purely qualitative measure to ensure that flow is generally passing through the test system, but this cannot identify smaller leaks that could still result in iodine loss.

Within 5 min of starting Test 5, the water-filled beaker indicated that gas was not exiting the system through the effluent line. The test was suspended, and the joints were reseated. This troubleshooting action appeared to resolve the issue, with gas flow observed upon test restart and persisting through test duration. It was noted that similar failures could have occurred in Tests 1–3 and without verification of effluent flow, these failures would have been undetected. Future testing will include a flow meter on the effluent line to provide a quantitative measure of flow through the test system.

3.2 CH_3I Adsorption on Ag^0Z

Both Tests 4 and 5 showed quantifiable recovery of iodine on the sorbent beds, with 31.1% ± 14.5 recovered for Test 4 and 98.2% ± 3.3 recovered for Test 5. Although the recovery for Test 4 was <100%, the test design did not require that 100% of iodine delivered be recovered, only that enough iodine was on each sample bed to assess the effect of sample removal procedures. Figures 3 and 4 compare the segment loading before and after vacuum removal for Tests 4 and 5, respectively. In each bed segment, it is observed that the iodine loading does not vary with the removal method (i.e., poured or vacuumed).

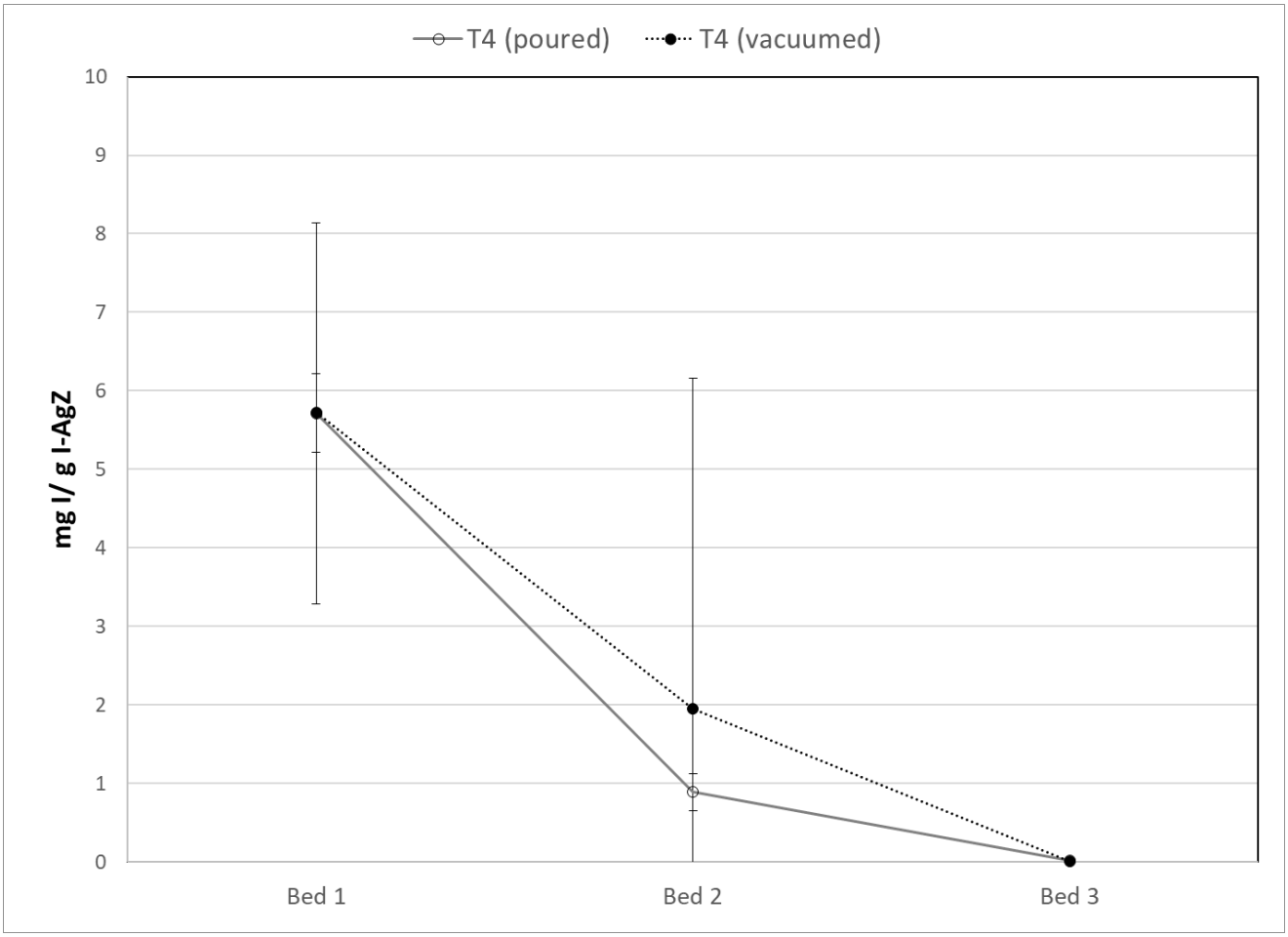

Figure 3. CH_3I adsorption on Ag^0Z, Test 4 [CH_3I = 200 ppb].

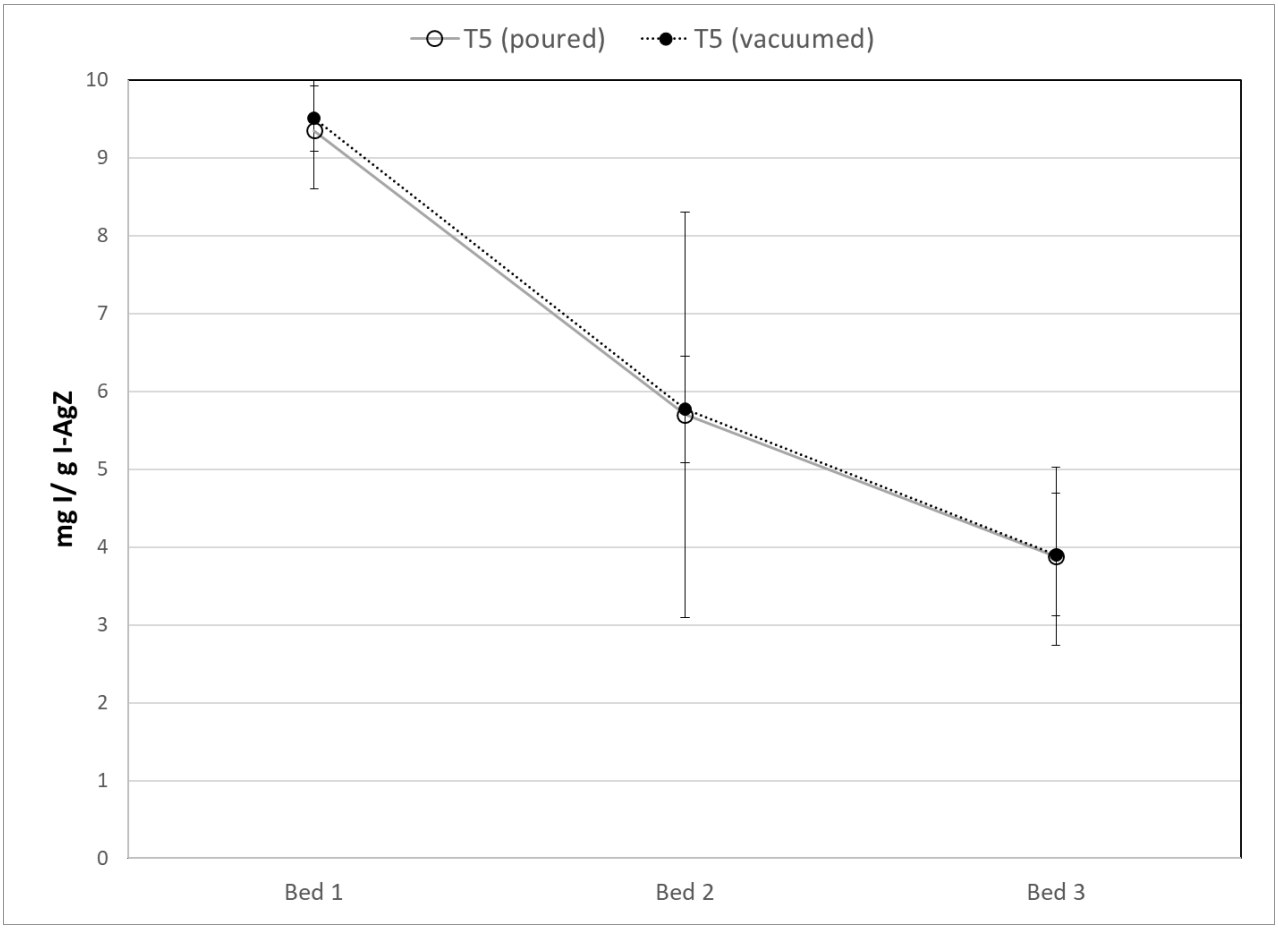

Figure 4. CH_3I adsorption on Ag^0Z, Test 5 [CH_3I = 200 ppb].

Tables 4 and 5 provide the results for each analyzed subsample for Tests 4 and 5, respectively. The average loading for each bed segment as a function of removal method is shown with a 95% confidence interval. The average loading and 95% confidence interval is also shown for all samples with no discrimination by removal method. This second value for iodine loading (averaged over all samples) was used to calculate the total iodine recovery on the sorbent beds. The maximum observed loadings (found in the first bed segments of each test) were 9.5 and 5.7 mg I/g I–Ag^0Z for Tests 4 and 5, respectively.

Table 4. Iodine loading for Test 4.

Sample ID	Iodine loading (mg I/g I-Ag^{0}Z)		
	Individual sample	Average loading of bed segment for each removal method[a]	Average loading of bed segment (all samples)[b]
VOG18-T4-Bed 1a	4.5926	5.71 ± 2.43	5.71 ± 0.97
VOG18-T4-Bed 1b	5.2045		
VOG18--T4-Bed 1c	7.3378		
VOG18-T4-Bed 1d-vac	5.6396	5.72 ± 0.50	
VOG18-T4-Bed 1e-vac	5.7991		
VOG18-T4-Bed 2a	1.0447	0.89 ± 0.24	1.31 ± 0.36
VOG18-T4-Bed 2b	0.8566		
VOG18-T4-Bed 2c	0.7663		
VOG18-T4-Bed 2d-vac	1.2799	1.95 ± 4.21	
VOG18-T4-Bed 2e-vac	2.6144		
VOG18-T4-Bed 3a	0.0129	0.02 ± 0.01	0.02 ± 0.01
VOG18-T4-Bed 3b	0.0217		
VOG18-T4-Bed 3c	0.0302		
VOG18-T4-Bed 3d-vac	0.0096	0.01 ± 0.03	
VOG18-T4-Bed 3e-vac	0.0178		

[a] Data used to determine effect of removal method on sample loading.
[b] Data used to determine iodine recoveries on sorbent beds.

Table 5. Iodine loading for Test 5.

Sample ID	Iodine loading (mg I/g I-Ag^{0}Z)		
	Individual sample	Average loading of bed segment for each removal method[a]	Average loading of bed segment (all samples)[b]
VOG18-PHYS5-Bed1-novac-a	9.8626	9.35 ± 0.75	9.36 ± 0.23
VOG18-PHYS5-Bed1-novac-b	9.1001		
VOG18-PHYS5-Bed1-novac-c	9.0873		
VOG18-PHYS5-Bed1-vac-a	9.7511	9.50 ± 0.42	
VOG18-PHYS5-Bed1-vac-b	9.2563		
VOG18-PHYS5-Bed1-vac-c	9.2550		
VOG18-PHYS5-Bed2-novac-a	6.1120	5.70 ± 2.60	5.73 ± 0.4
VOG18-PHYS5-Bed2-novac-b	5.2864		
VOG18-PHYS5-Bed2-vac-a	5.6602	5.77 ± 0.68	
VOG18-PHYS5-Bed2-vac-b	5.8769		
VOG18-PHYS5-Bed3-novac-a	3.6989	3.88 ± 1.14	3.89 ± 0.19
VOG18-PHYS5-Bed3-novac-b	4.0601		
VOG18-PHYS5-Bed3-vac-a	3.7749	3.90 ± 0.79	
VOG18-PHYS5-Bed3-vac-b	4.0254		

[a] Data used to determine effect of removal method on sample loading.
[b] Data used to determine iodine recoveries on sorbent beds.

3.3 Elemental iodine (I_2)

Concurrent to the execution of this testing, an experiment characterizing I_2 adsorption by Ag^{0}Z under VOG conditions was completed (Jubin 2018). In that experiment, the mass balance for iodine closed within 2%, which is within the expected combined uncertainty of the delivery rate and analytical error. Vacuum removal was used to remove discrete bed segments. The successful closure of the mass balance indicated that no measurable iodine (presented to the sorbent as I_2) was removed by vacuum.

4. CONCLUSIONS

Duplicate tests showed that no quantifiable amount of adsorbed iodine (fed as CH_3I) was removed by vacuum during sampling when Ag^{0}Z is not approaching saturation. In six bed segments analyzed (three bed segments per test), none displayed variation in total iodine loading as a result of vacuum removal. Previously reported testing indicates that vacuum removal will also not affect adsorbed iodine on Ag^{0}Z when it is fed as I_2. These results indicate that the incomplete recovery of iodine on silver-based sorbent beds previously observed by the authors is not an artifact of the sample removal method.

During testing, it was determined that the glass columns supporting the sorbent beds may allow loss of iodine from the system. Future work will ensure that these leak points are minimized or eliminated. Quantitative monitoring of effluent flow will further verify the iodine flow rate through the sorbent columns.

The determination that vacuum removal does not affect measured iodine loading is encouraging. It provides assurance that the iodine adsorbed by Ag^{0}Z, in either organic or inorganic forms, is likely tightly bound and

will remain immobilized during sorbent usage and light handling that might occur during waste processing. Future testing should determine whether this finding extends to saturated sorbents.

5. REFERENCES

Anderson, KK, SH Bruffey, DL Lee, RT Jubin, and JF Walker. 2012. Iodine Loading of Partially Reduced Silver Mordenite. Report No. FCRD-SWF-2013-000079. US Department of Energy Separations and Waste Forms Campaign, December 28.

Bruffey, SH, RT Jubin, and JA Jordan. 2016a. Organic Iodine Adsorption by AgZ under Prototypical Vessel Off-Gas Conditions. Report Nos. FCRD-MRWFD-2016-000357, ORNL/TM-2016/568. Oak Ridge National Laboratory, Oak Ridge, TN.

Bruffey, SH, RT Jubin, and JA Jordan. 2016b. Organic Iodine Adsorption by Ag-Aerogel under Prototypical Vessel Off-Gas Conditions. Report Nos. FCRD-MRWFD-2016-000312, ORNL/TM-2016/417. Oak Ridge National Laboratory, Oak Ridge, TN, 2016.

Jubin, RT, NR Soelberg, D Strachan, and G Ilas. 2012. Fuel Age Impacts on Gaseous Fission Product Capture During Separations. Report Nos. FCRD-SWF-2012-000089, PNNL-22550. Oak Ridge National Laboratory, Oak Ridge, TN.

Jubin, RT, DM Strachan, NR Soelberg, and G Ilas. 2013. Iodine Pathways and Off-Gas Stream Characteristics for Aqueous Reprocessing Plants—A Literature Survey and Assessment. Report No. FCRD-SWF-2013-000308. Oak Ridge National Laboratory, Oak Ridge, TN.

Jubin, RT, SH Bruffey, and BB Spencer. 2015. Performance of Silver-exchanged Mordenite for Iodine Capture under Vessel Off-gas Conditions. Proceedings of Global 2015. September.

Jubin, RT, JA Jordan, and SH Bruffey. 2017. Performance of Silver-Exchanged Mordenite and Silver-functionalized Silica-Aerogel under Vessel Off-gas Conditions. Report No. ORNL/TM-2017/477. Oak Ridge National Laboratory, Oak Ridge, TN. September.

Jubin, RT, JA Jordan, and SH Bruffey. 2018. Extended Elemental Iodine Adsorption by AgZ under Prototypical Vessel Off-Gas Conditions. Report Nos. NTRD-MRWFD-2018-000211, ORNL/SPR-2018/884. Oak Ridge National Laboratory, Oak Ridge, TN.

Nenoff, TM, MA Rodriguez, NR Soelberg, and KW Chapman. 2014. “Silver-Mordenite for Radiologic Gas Capture from Complex Streams: Dual Catalytic CH_3I Decomposition and I Confinement.” *Microporous Mesoporous Materials* 200: 297–303.