Methyl Iodide Adsorption Test Results

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SUMMARY

Of the four volatile radionuclides that may require removal from the off-gas streams of a US-sited used nuclear fuel reprocessing plant (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I), ^{129}I is expected to require the greatest efficiency of removal. Historically, the removal of organic iodine species has been considered more difficult than the removal of elemental iodine (I_2). In 2012, Oak Ridge National Laboratory (ORNL), Idaho National Laboratory (INL), Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratory (SNL) released a joint test plan designed to better understand the adsorption of organic iodine, specifically methyl iodide (CH_3I) by silver mordenite (AgZ).

Repeated observations by INL have confirmed the presence of elemental iodine (I_2) in the effluent of AgZ deep beds, even though methyl iodide (CH_3I) is the sole iodine species in the feed gas. The intent of the joint test plan was to identify key questions about the behavior of CH_3I when adsorbed by AgZ and to ensure that previously observed INL data were validated by duplicate testing. The test plan was expected to proceed through multiple stages, and the purpose of this report is to document the results of Phase 1 testing prescribed by the joint test plan, which was conducted at ORNL. INL has reported its corresponding test results, and synthesis of ORNL and INL results is expected to be completed in the near future. The forthcoming report will answer some of the questions identified by the joint test plan.

Seven thin bed tests characterizing the adsorption of CH_3I and I_2 by AgZ and NaZ were performed. The first three tests examined the effects of NO_X and H_2O on CH_3I adsorption by AgZ and found that a 43% reduction in iodine capacity occurred when NO_X was present in the feed stream (as compared to CH_3I adsorption from a dry air stream) and that a 23% reduction in iodine capacity occurred when both NO_X and H_2O were present in the feed stream.

Four of these thin bed tests compared the adsorption of I_2 and CH_3I by NaZ and AgZ. As expected, adsorbed iodine was bound strongly to AgZ and was not removed during the purge phase of testing. This was in contrast to I_2 and CH_3I sorption by NaZ, in which significant weight loss was observed during the purge phase of testing. NaZ did retain some CH_3I (33 mg/g I-NaZ) under the test conditions chosen (CH_3I capacity of AgZ is 75 mg/g I-AgZ). However, CH_3I may not have been fully removed from the NaZ, as evidenced by the slow purge rate, so the final CH_3I capacity of NaZ may be an overestimate. Given these data, it was found that 51% of the CH_3I adsorbed by NaZ during loading was retained by the sorbent during the dry air purge, and interactions between CH_3I and the zeolite mineral are believed to be significant in the mechanism of CH_3I adsorption by AgZ.

The data reported here are intended to be synthesized with the data obtained by INL in fulfillment of the joint test plan. The combined data are expected to provide fundamental insight into the adsorption mechanism of CH_3I by AgZ as well as supply practical information for use in engineering designs needed for iodine abatement systems in used nuclear fuel reprocessing plants.

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ACRONYMS

AgZ	silver-exchanged mordenite
INL	Idaho National Laboratory
NAA	neutron activation analysis
NaZ	sodium mordenite
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
SNL	Sandia National Laboratory
TGA	thermogravimetric analyzer

METHYL IODIDE ADSORPTION TEST RESULTS

1. INTRODUCTION

Of the four volatile radionuclides that may require removal from the off-gas streams of a US-sited used nuclear fuel reprocessing plant (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I), ^{129}I is expected to require the greatest efficiency of removal (Jubin et al. 2012a). Within the reprocessing plant it is expected that iodine will be released into off-gas streams from multiple unit operations (including dissolution, solvent extraction, and waste processing). Each of these off-gas streams will contain iodine in different chemical forms, will have different flow rates, different moisture levels, and may contain minor constituents such as NO_X that are known to be corrosive. It is likely that each of these streams will require iodine removal in order to meet stringent US regulatory limits. For the last 10 years, the Office of Nuclear Energy within the US Department of Energy has funded a multilaboratory collaboration focused on the treatment of off-gas streams from used nuclear fuel processing, and significant advancements have been made in the understanding of volatile radionuclide management during this research program.

Historically, the removal of organic iodine species has been considered more difficult than the removal of elemental iodine (I_2). Roughly 5% of the iodine released during fuel dissolution is expected to be organic in nature, and iodine released from solvent extraction operations is expected to be composed of up to 50% organic iodine species (Jubin et al. 2013). In 2012, Oak Ridge National Laboratory (ORNL), Idaho National Laboratory (INL), Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratory (SNL) released a joint test plan designed to better understand the adsorption of organic iodine, specifically methyl iodide (CH_3I) by silver mordenite (AgZ) (Jubin et al. 2012b). Silver mordenite is a zeolite mineral containing silver within the zeolite framework and is considered a reference adsorbent for iodine in this application because it has been studied extensively.

Repeated observations by INL have confirmed the presence of elemental iodine (I_2) in the effluent of AgZ deep beds, despite the sole iodine species in the feed gas being methyl iodide (CH_3I). Most notably, Haefner and Watson (2010) observed that upon test initiation, 95% of the iodine found in the effluent was in the form of CH_3I, whereas after column breakthrough less than 5% was CH_3I, with I_2 comprising the balance. This presumed conversion of CH_3I to I_2 in the presence of AgZ has been the subject of continued study, with a proposed mechanism reported in Nenoff et al. (2014). The earliest reports of this phenomena date to the 1970s. The intent of the joint test plan was to identify key questions about the behavior of CH_3I when adsorbed by AgZ and to ensure that previously observed INL data were validated by duplicate testing. The test plan was expected to proceed through multiple stages, and the purpose of this report is to document the results of Phase 1 testing prescribed by the joint test plan and conducted at ORNL. INL has reported its corresponding test results, and synthesis of ORNL and INL results is expected to be completed in the near future. The forthcoming report will answer some of the questions identified by the joint test plan (Soelberg and Watson, 2014a and 2014b).

2. JOINT TEST PLAN DESCRIPTION

Two primary questions were posed in the joint test plan:

1) What are the iodine-bearing and organic species present in the effluent from an AgZ deep bed exposed to a methyl iodide-bearing feed stream?
2) What is the origin of elemental iodine in the effluent stream? Possible sources could include gas-phase reactions, adsorption reactions, or decomposition catalyzed by the mordenite substrate.

The test plan was structured such that INL was to perform a series of deep bed testing focused on answering question 1, and ORNL would perform thin bed testing under corresponding conditions.

Together, these tests would characterize multiple aspects of methyl iodide adsorption by AgZ, including monitoring the effluent gas composition, adsorption rate, and observed iodine capacity. Table 1 shows the conditions for the three thin bed tests to be completed by ORNL.

Table 1. Thin bed testing characterizing CH_3I adsorption by AgZ as prescribed in the joint test plan.

Iodine speciation and concentration *(ppmv)*	Temperature *(°C)*	Gas velocity *(m/min.)*	Humidity of feed stream *(wt% H_2O)*	NO concentration *(ppmv)*	NO_2 concentration *(ppmv)*
CH_3I, 33	150	4.3	2	833	833
CH_3I, 33	150	4.3	0	833	833
CH_3I, 33	150	4.3	0	0	0

The second question, which was designed to understand the effects of iodine speciation and the zeolite substrate on iodine adsorption by AgZ, was to be answered through a series of thin bed tests exposing silver-free and silver-bearing mordenite to both I_2 and CH_3I-bearing feed streams. These tests are described in Table 2. Each of these tests were conducted at a temperature of 150°C, a gas velocity of 10 m/min., and an iodine concentration of either 50 ppmv (for I_2) or 50 ppmv (for CH_3I). NO, NO_2, and water were not present in the feed streams. NaZ refers to silver-free mordenite, which contains sodium as the cation within the zeolite mineral framework.

Table 2. Thin bed testing designed to understand the effects of iodine speciation and zeolite substrate on iodine adsorption by AgZ.

Iodine speciation	Sorbent
I_2	NaZ
CH_3I	NaZ
I_2	AgZ
CH_3I	AgZ

To augment both types of testing, an examination of data available for gas-phase reactions of relevant species was performed, and the results are included in this document.

3. MATERIALS AND SYSTEMS

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 had a measured bulk density of 0.84 g/cm^3 and a maximum I_2 capacity of 86 mg/g I-AgZ at conditions used in testing.

Thin bed testing of methyl iodide adsorption by AgZ was performed using a custom-built thermogravimetric analyzer (TGA) (Figure 1). A thin bed of sorbent material (<2 g total weight) was contained within a temperature-controlled oven. This TGA is designed to weigh the sorbent continuously as the sorbent is exposed to a dry gas stream bearing analytes of interest, in this case methyl iodide. Humid air, NO, and NO_2 were added to the feed gas as specified by the joint test plan. The TGA allows for the iodine loading of the sorbent to be observed in real-time. Once the weight gain was observed to be less than 5 mg/g for a 24 hour period, the sorbent was assumed to be saturated. It was then purged with dry air for 24 hours to remove any physisorbed iodine.

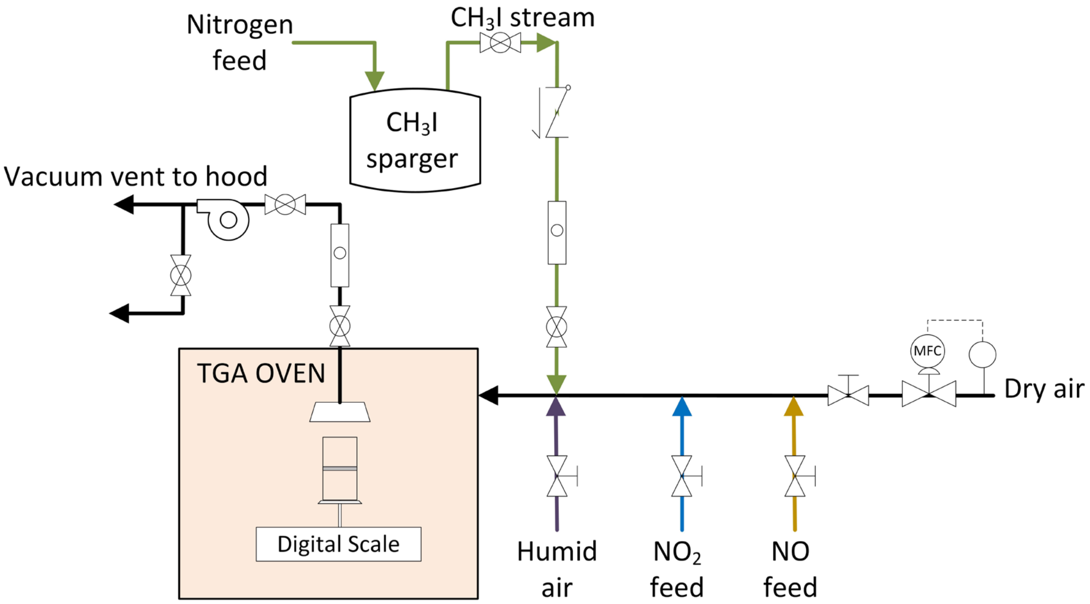

Figure 1. ORNL TGA.

A CH_3I-bearing feed stream was generated by sparging liquid CH_3I with N_2 at a known flow rate. The CH_3I was stored in a freezer at −33°C to depress the vapor pressure to the levels required for this testing. NO gas was procured commercially. NO_2 was produced through oxidation of NO by air. Expected conversion to NO_2 is 95–98% given the residence time and reagent concentrations within the experimental system, but the precise NO_2 concentration was not confirmed during this testing. Humid air was generated by sparging liquid water with a dry gas stream at a known flow rate and temperature.

After iodine loading, the samples were each removed from the system by vacuum and transferred to ORNL's High Flux Isotope Reactor for neutron activation analysis (NAA) of adsorbed iodine.

4. RESULTS

In addition to the experimental results reported in Sections 4.2 and 4.3, a brief summary of relevant literature is provided in Section 4.1 to assist in better understanding the chemical reactions that may be associated with CH_3I adsorption by AgZ.

4.1 Published Thermodynamic and Experimental Studies

One of the earliest reports of the presence of I_2 in the effluent of AgZ deep beds (with the feed gas containing only organic iodine species) is that of Scheele et al. (1983). This study attempted to resolve the effects of gas velocity, temperature, NO_X concentration, H_2O concentration, and physical properties of the sorbent on the adsorption of CH_3I by AgZ. Additionally, they compiled several relevant reactions to determine their thermodynamic favorability. Representative reactions are provided in Table 3. In the same study, partial oxidation of CH_3I was confirmed by the observation of methanol and dimethyl ether in the effluent of adsorption testing.

Table 3. Relevant chemical reactions tabulated from Scheele et al. (1983).

Eqn. no.	Reaction	ΔG (400K) *kJ/mol Ag*
1	$2Ag + 2CH_3I(g) \rightarrow 2AgI + C_2H_6$	−98
2	$Ag + CH_3I(g) + H_2O(g) \rightarrow AgI + CH_3OH(g) + ½ H_2$	−32
3	$7NO + 2 CH_3I(g) \rightarrow I_2(g) + 2CO_2 + 3H_2O(g) + 7/2 N_2$	−1,079
4	$7NO_2 + 4 CH_3I(g) \rightarrow I_2(g) + 4CO_2 + 6H_2O(g) + 7/2 N_2$	−853

Equations 3 and 4 show that the presence of NO_X can catalyze the degradation of CH_3I to I_2, with I_2 being more readily absorbed by AgZ. This would support the observation made by Haefner and Watson (2010) of the presence of elemental iodine in the effluent stream of similar deep bed testing.

Further thermodynamic predictions were performed by Bruffey et al. (2015), and two key reactions shown in Table 4.

Table 4. Relevant chemical reactions tabulated from Bruffey et al. (2015) using the equation $\Delta G = -RT\,ln(K)$.

Eqn. #	Reaction	ΔG (298K) *kJ/mol*
5	$2CH_3I(g) + 2NO_2(g) \rightarrow 2CH_3NO_2(g) + I_2(g)$	−146
6	$2CH_3NO_2 + CH_3I(g) \rightarrow CH_3OCH_3 + NOI(g)$	−9.6

Importantly, Equations 5 and 6 provide a pathway for the formation of dimethyl ether, which was reported by Scheele et al. (1983) in the effluent of CH_3I deep bed adsorption studies.

The reviewed literature indicates the interactions of CH_3I, NO_X, I_2, silver, and the mordenite substrate are complex and likely governed by multiple reaction pathways. One of the more recent and detailed studies focused on the mechanism of CH_3I sorption by AgZ was reported by Nenoff et al. (2014). This study specifically monitored for organic species present in the effluent of AgZ deep beds with CH_3I-bearing feed gas streams and found dimethyl ether, methyl nitrite, and methanol in the effluent. This increases the likelihood that CH_3I is being converted as indicated by Equations 2, 5 and 6. Additionally, Nenoff et al. (2014) postulated that CH_3I was interacting with the zeolite substrate itself and may be forming similar organic by-products during that reaction.

4.2 Thin Bed Testing of CH_3I Adsorption by AgZ

The data obtained from the testing detailed in Table 1 are shown in Figure 2. The measured weight gain of the sorbent before and after the dry air purge is shown in Table 5, along with the iodine content of the loaded sorbent measured by NAA. The presence of NOx was observed to increase the initial loading rate compared to loading from a CH_3I-bearing dry air stream. Some of this initial weight gain may be attributable to adsorption of NO or NO_2 by the zeolite, but this cannot be resolved by weight measurements. Testing with water and NO_X in the feed stream showed the same early rapid weight gain. Note that water adsorption of 10–20 mg/g loaded sorbent is expected at 150°C, based on previous testing at ORNL.

The early adsorption rate of the NOx and NO_X/H_2O tests also corresponded with earlier sorbent saturation times, with adsorption of CH_3I from a dry air stream requiring roughly double the loading time to achieve sorbent saturation (150 h vs. 300 h). However, the iodine saturation capacity of the sorbent was significantly higher (93.1 mg/g I-AgZ) when adsorbing CH_3I from a dry air stream as compared to adsorption from a NO_X or NO_X/H_2O-bearing feed stream (39.5 and 71.3 mg/g I-AgZ, respectively). Thus, the presence of NOx in the feed stream appears to decrease the sorbent iodine capacity. These numbers also indicate that the presence of H_2O in the feed stream may limit the decrease in sorbent iodine capacity due to the presence of NO_X in the feed stream.

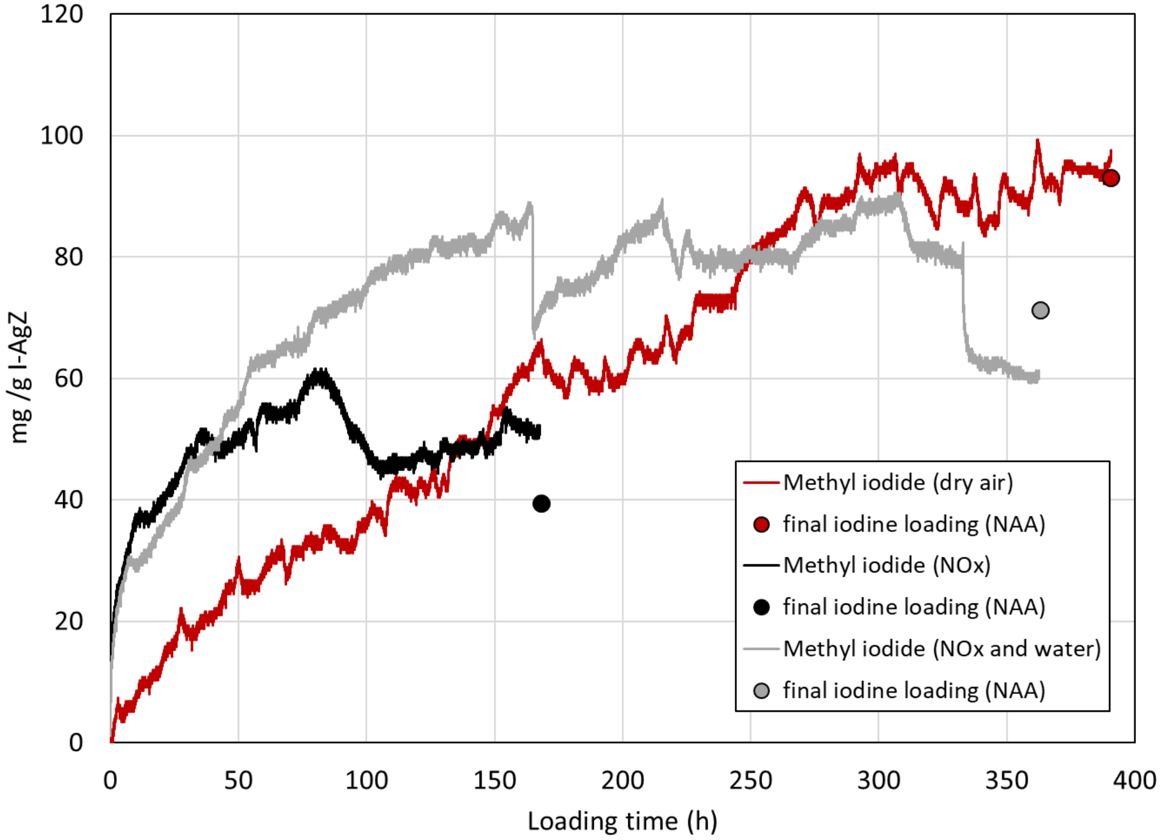

Figure 2. Adsorption of CH_3I by AgZ from varying feed gas compositions.

Table 5. Observed weight gain and confirmed iodine loading of CH_3I thin bed tests.

Gas composition	Weight gain* (before purge)	Retained weight (after purge)*	Iodine loading determined by NAA
	mg/g loaded sorbent		*mg I/g I-AgZ*
CH_3I in dry air	97	97	93.1 ± 2.6
CH_3I in NO_X	50	51	39.5 ± 1.1
CH_3I in NO_X, H_2O	71	61	71.3 ± 2.0
*Determined by TGA observations			

4.3 Thin Bed Testing of Speciation and Substrate Impacts on Iodine Adsorption by AgZ

The data obtained from the testing detailed in Table 2 is shown in Figures 3–6. The measured weight gain of the sorbent before and after the dry air purge is shown in Table 6, along with the iodine content of the loaded sorbent measured by NAA.

Notably, limited weight loss (presumed to be physisorption of the iodine species) occurred during the dry air purge of AgZ, but significant weight loss was observed during the purge of NaZ. Additionally, the total weight loss from NaZ during the dry air purge was less with CH_3I as the sorbate (51%) vs. I_2 as the sorbate (73%). This may indicate that the CH_3I interacts more strongly with the mordenite substrate than does I_2 and would support the mechanisms postulated by Nenoff et al. (2014). Additionally, the initial adsorption rate of CH_3I onto NaZ was significantly higher than that of I_2 (Figure 5).

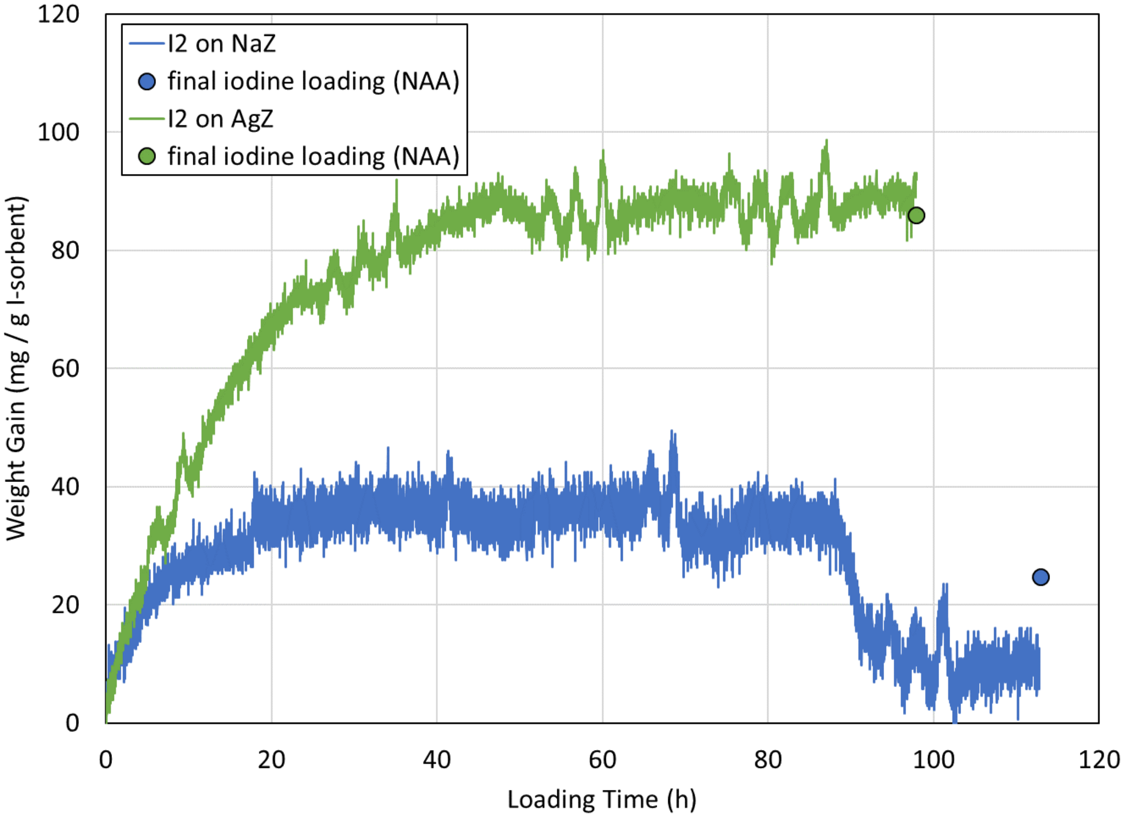

Figure 3. Adsorption of I_2 by NaZ and AgZ.

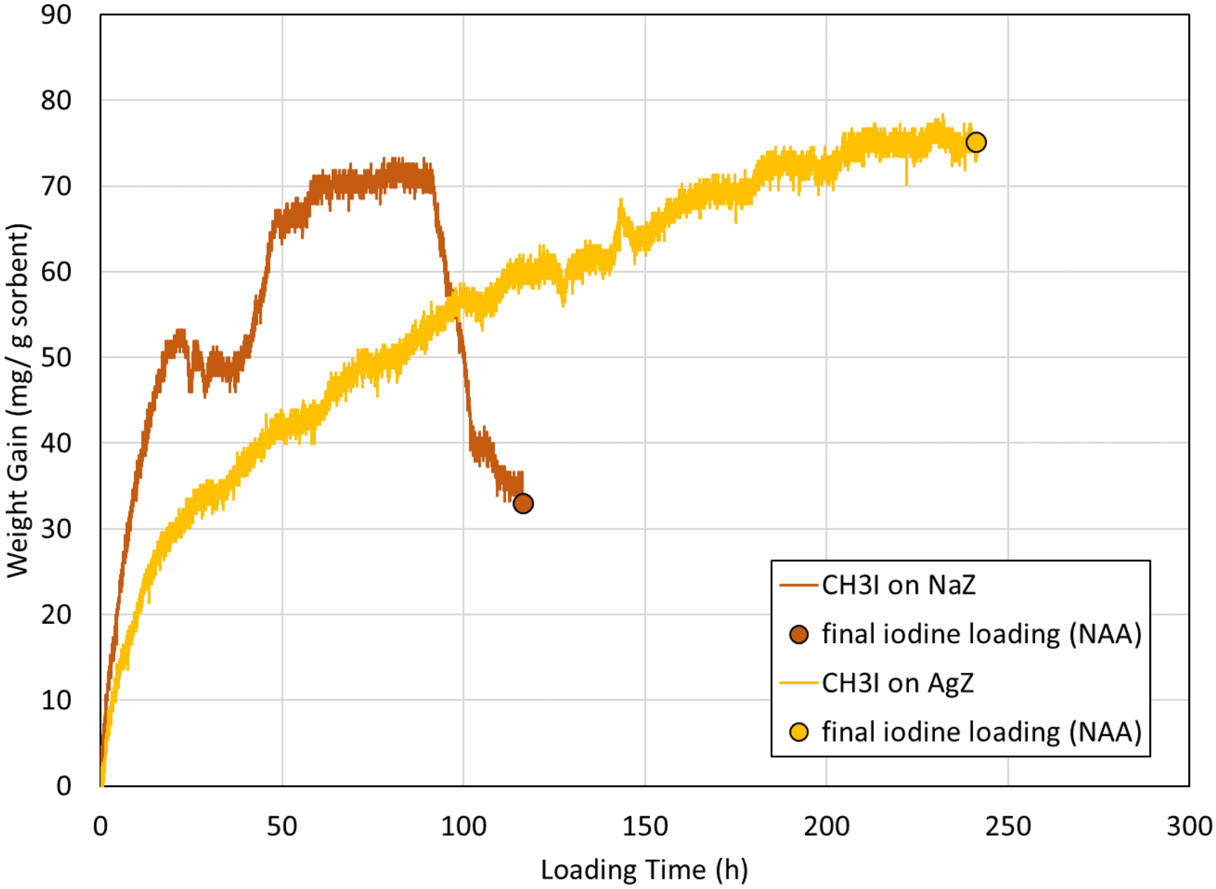

Figure 4. CH_3I adsorption by NaZ and AgZ.

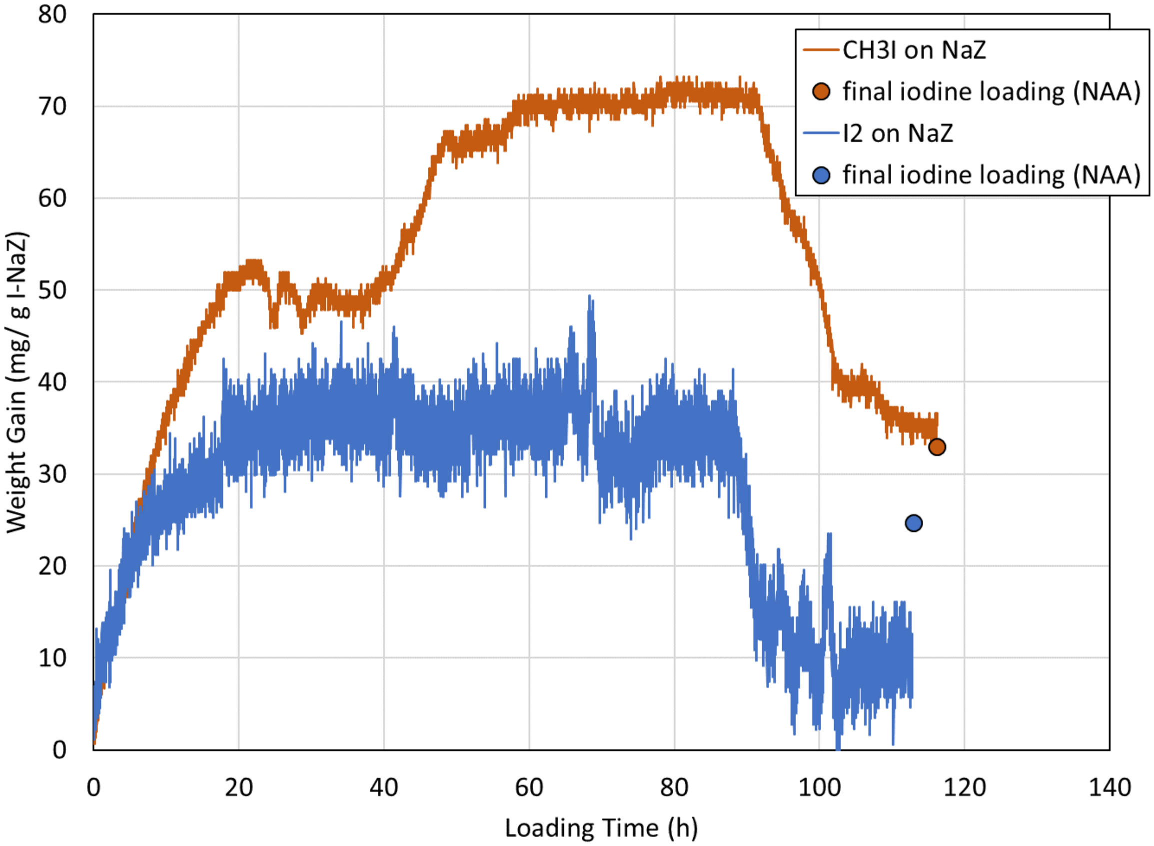

Figure 5. Adsorption of I_2 and CH_3I by NaZ.

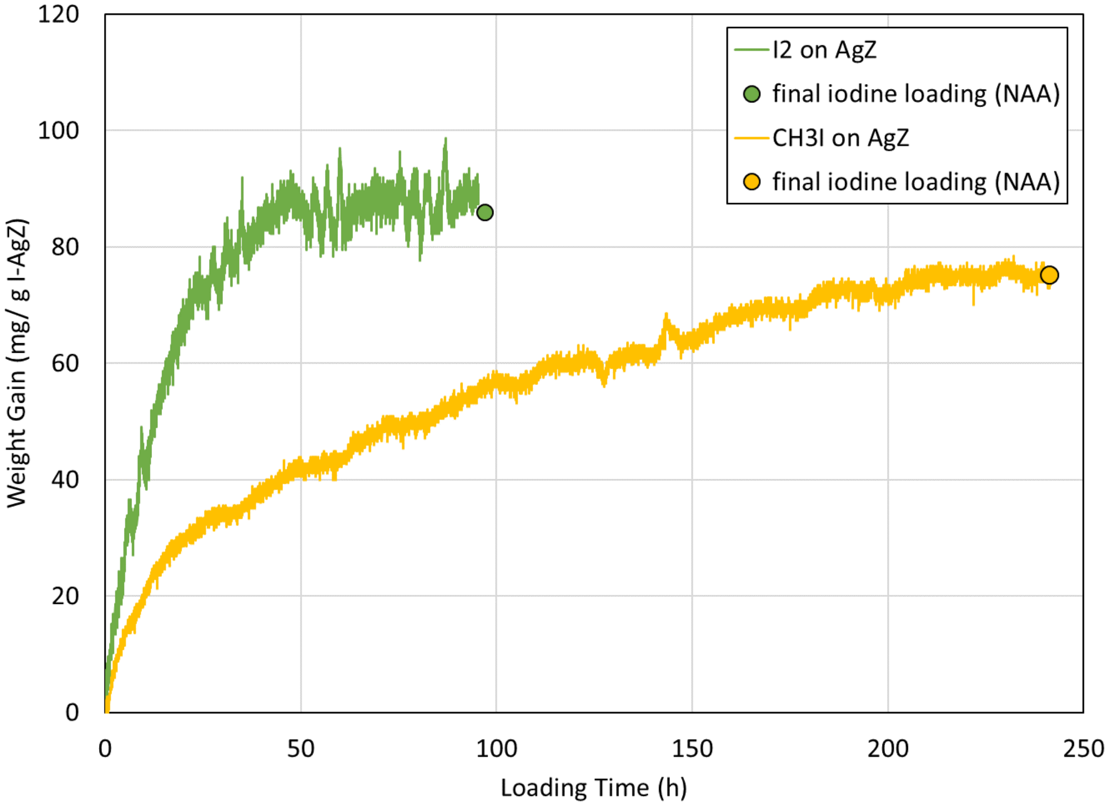

Figure 6. Adsorption of I_2 and CH_3I by AgZ.

Table 6. Comparison of I_2 and CH_3I loadings for AgZ and NaZ.

Sorbent/ iodine species	Weight gain(before purge)*	Retained weight (after purge)*	Weight loss (during purge)*	Iodine loading determined by NAA	Difference in iodine loading determined by NAA and weight gain by TGA
	(mg/g loaded sorbent)		*%*	*(mg/g I-AgZ)*	
NaZ/I_2	35	10	73%	24.7 ± 0.7	+14.7
NaZ/CH_3I	71	35	51%	33.0 ± 0.9	-2.0
AgZ/I_2	90	88	< 5%	86.0 ± 2.4	-2.0
AgZ/CH_3I	75	74	< 5%	75.2 ± 2.1	+1.2
* *As determined by TGA observations*					

Data from testing with NaZ/I_2 showed a difference between the measured weight gain of the sorbent and the iodine loading of the sorbent as measured by NAA. This difference was not observed with the other tests, so this result should be verified by further testing.

5. SUMMARY AND CONCLUSIONS

Planned tests conducted at ORNL in fulfillment of Phase I of the joint test plan prepared by ORNL, INL, PNNL, and SNL have been completed. Seven thin bed tests characterizing the adsorption of CH_3I and I_2 by AgZ and NaZ were performed. The first three tests examined the effects of NO_X and H_2O on CH_3I adsorption by AgZ and found that a 43% reduction in iodine capacity occurred when NO_X was present in the feed stream (as compared to CH_3I adsorption from a dry air stream) and that a 23% reduction in iodine capacity occurred when both NO_X and H_2O were present in the feed stream. Ongoing testing at ORNL includes statistically resolving the effects of H_2O and NO_X on CH_3I adsorption by AgZ, and that work is expected to be reported in early 2020.

Four thin bed tests compared the adsorption of I_2 and CH_3I by NaZ and AgZ. As expected, adsorbed iodine was bound strongly to AgZ and was not removed during the purge phase of testing. This was in contrast to I_2 and CH_3I sorption by NaZ, in which significant weight loss was seen during the purge phase of testing. It was noted that NaZ did retain some CH_3I (33 mg/g I-NaZ) under the test conditions chosen (CH_3I capacity of AgZ is 75 mg/g I-AgZ). However, CH_3I may not have been fully removed from the NaZ as evidenced by the slow purge rate shown in Figure 5, so the final CH_3I capacity of NaZ may be an overestimate. Given these data, it was found that 51% of the CH_3I sorbed by NaZ during loading was retained by the sorbent during the dry air purge, and interactions between CH_3I and the zeolite mineral may be significant in the mechanism of CH_3I adsorption by AgZ. This is supported by studies performed at INL and SNL.

The data reported here are intended to be synthesized with the data obtained by INL in fulfillment of the joint test plan. The combined data are expected to provide fundamental insight into the adsorption mechanism of CH_3I by AgZ as well as supply practical information for use in engineering designs needed for iodine abatement systems in used nuclear fuel reprocessing plants.

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