

Organic Iodine Adsorption by AgZ under Prototypical Vessel Off-Gas Conditions

Fuel Cycle Research & Development

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SUMMARY

U.S. regulations will require the removal of ^{129}I from the off-gas streams of any used nuclear fuel (UNF) reprocessing plant prior to discharge of the off-gas to the environment. Multiple off-gas streams within a UNF reprocessing plant combine prior to release, and each of these streams contains some amount of iodine. For an aqueous UNF reprocessing plant, these streams include the dissolver off-gas, the cell off-gas, the vessel off-gas (VOG), the waste off-gas and the shear off-gas. To achieve regulatory compliance, treatment of multiple off-gas streams within the plant must be performed.

Preliminary studies have been completed on the adsorption of I_2 onto silver mordenite (AgZ) from prototypical VOG streams. The study reported that AgZ did adsorb I_2 from a prototypical VOG stream, but process upsets resulted in an uneven feed stream concentration. The experiments described in this document both improve the characterization of I_2 adsorption by AgZ from dilute gas streams and further extend it to include characterization of the adsorption of organic iodides (in the form of CH_3I) onto AgZ under prototypical VOG conditions. The design of this extended duration testing was such that information about the rate of adsorption, the penetration of the iodine species, and the effect of sorbent aging on iodine removal in VOG conditions could be inferred.

It was found that I_2 penetrated an AgZ sorbent bed to a depth of 2.2 cm. As sorbent time online increased, the rate of iodine adsorption appeared to decrease. This supports the existence of AgZ aging that affects I_2 adsorption. It was observed that CH_3I penetrated into the first 2.4 cm of an AgZ sorbent bed. No sorbent aging effects were observed for the CH_3I adsorption testing. A qualitative observation of the differences in adsorption behavior for the two species reveals that the rate of I_2 adsorption was twice that of CH_3I adsorption. The decontamination factors for these systems were not able to be determined as no measurable iodine was observed in the bed effluent.

Future efforts regarding the adsorption of iodine from prototypical vessel off-gas streams by silver-based sorbents will attempt to resolve some of the questions raised here, both regarding mass balance and the effect of aging on iodine adsorption by AgZ from a dilute gas stream, as it appears that aging may present differently for different iodine species. Additionally, the adsorption of longer-chain organic iodine species, such as $\text{C}_{12}\text{H}_{25}\text{I}$ will be studied. Other variables that merit examination are the gas velocity of the test and the dependence of the observed results on the inlet iodine concentration. Finally, longer duration testing should be considered in an effort to determine the mass transfer zone and decontamination factors associated with iodine adsorption by AgZ under prototypical vessel off-gas conditions.

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ACRONYMS

AgZ	Silver mordenite
Ag ⁰ Z	Reduced silver mordenite
COG	Cell off-gas
DF	Decontamination factor
DOG	Dissolver off-gas
NAA	Neutron activation analysis
ORNL	Oak Ridge National Laboratory
UNF	Used nuclear fuel
VOG	Vessel off-gas

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ORGANIC IODINE ADSORPTION BY AgZ UNDER PROTOTYPICAL VESSEL OFF-GAS CONDITIONS

1. INTRODUCTION

U.S. regulations will require the removal of ^{129}I from the off-gas streams of any used nuclear fuel (UNF) reprocessing plant prior to discharge of the off-gas to the environment. The release of volatile radioactive iodine is governed by three regulations in the United States (40 CFR 61, 40 CFR 190, and 10 CFR 20). These regulations govern both total release limits for iodine and the potential combined dose from the four volatile radionuclides of most concern for reprocessing (^3H , ^{14}C , ^{85}Kr , and ^{129}I). The required plant decontamination factor (DF) for iodine will vary based on fuel burnup, cooling time, and other factors but is very likely to be >1000 and could be as high as 8000 (Jubin 2012).

Multiple off-gas streams within a UNF reprocessing plant combine prior to environmental release, and each of these streams contains some amount of iodine. For an aqueous UNF reprocessing plant, these streams include the dissolver off-gas (DOG), the cell off-gas (COG), the vessel off-gas (VOG), the waste off-gas and the shear off-gas. As 95-98% of the total iodine inventory of UNF is released to the DOG, complete removal of iodine from the DOG without treatment of other streams would result in a plant DF of <100 (Jubin 2013). Thus, to achieve regulatory compliance, treatment of multiple off-gas streams within the plant must be performed; specifically those such as the VOG where iodine concentration is low.

This conclusion motivates the investigation of iodine removal from the VOG. Vessel off-gas refers to the gas venting all chemical process tanks and equipment in the primary (non-waste) process line downstream of dissolver operations, including the solvent extraction operations that occur during aqueous UNF reprocessing. Any volatile components present in the solvent extraction vessels can transfer to this gas. The VOG will most likely contain iodine at ppb concentrations. It is possible that organic solvents will be present, along with some of their radiolytic degradation products. The VOG is also the stream most likely to contain organic iodides, which commonly are considered more difficult to remove with traditional sorbents than elemental iodine (I_2) (Bruffey et al. 2015a).

Preliminary studies have been completed on the adsorption of I_2 onto silver mordenite (AgZ) from prototypical VOG streams (Jubin et al. 2015). The study reported that AgZ did adsorb I_2 from a prototypical VOG stream, but process upsets resulted in an uneven feed stream concentration. The experiments described in this document both improve the characterization of I_2 adsorption by AgZ from dilute gas streams and further extend it to include characterization of the adsorption of organic iodides (in the form of CH_3I) onto AgZ under prototypical VOG conditions.

2. MATERIALS AND METHODS

2.1 Experimental materials

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16). It contains 11.9% silver by weight and has a 0.16 cm pellet diameter. Prior to use in testing, the sorbent material was reduced by extended exposure to a hydrogen/nitrogen blend gas at elevated temperature. Details of this procedure can be found in Anderson et al., 2012.

As iodine can be corrosive, especially in the presence of water, the materials of construction for the system were carefully selected to minimize iodine loss to system components and piping. The sorbent

beds were contained within glass columns (internal diameter = 3.45 cm) and separated by glass frits. The humid air and iodine supply streams were piped through separate lines of 316 stainless steel tubing. The two streams were blended together in a glass tee directly prior to introduction into the sorbent bed.

2.2 Test Conditions

Two tests were performed. The first examined the adsorption of I₂ onto Ag⁰Z and the second of CH₃I onto Ag⁰Z. The feed stream consisted of iodine in a moist air stream with a dew point of 0 °C. In I₂ adsorption test, the iodine stream was generated by a KinTek Flexstream Gas Standards Generator with an iodine injection rate of 524 ng/min and was at a concentration of 7 ppb in the diluted air stream. In the CH₃I adsorption test, the concentration of CH₃I was 40 ppb and was supplied from a compressed-gas cylinder containing 1000 ppm CH₃I (bal. N₂) gas blend. The sorbent beds were held at 150 °C, and the gas stream was preheated to 150 °C prior to contact with the sorbent beds. A superficial gas velocity of 10 m/min was calculated by using the empty column diameter of 3.45 cm.

2.3 Testing Protocol

The test system was designed with three sorbent beds placed in series. The first bed (Bed 1) was a thin bed with an approximate sorbent depth of 0.30 cm, which is equivalent to approximately two pellets of Ag⁰Z. This test bed was segmented into quadrants. The quadrants and test system are shown in Figure 1. Bed 1 was intended to measure the adsorption rate of iodine onto the sorbent during the test period by removing and replacing sorbent material from the quadrants at selected time intervals. The second sorbent bed (Bed 2) was approximately 11.0 cm deep, and the sorbent remained online for the duration of testing. Bed 2 was intended to measure the depth of the mass transfer zone for the conditions used during testing. The third bed (Bed 3) was 0.65 cm deep and was periodically removed and replaced throughout the test. Bed 3 was intended to detect breakthrough. The online time for each sorbent bed or quadrant during the I₂ adsorption test is shown in Table 1 and is shown for the CH₃I adsorption test in Table 2.

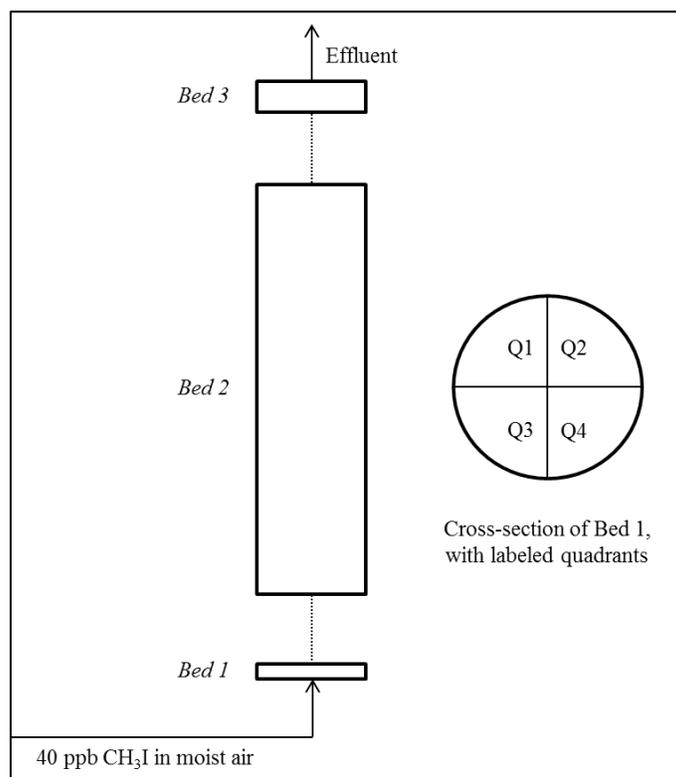


Figure 1: Schematic of test system

Table 1: Sampling protocol for I₂ adsorption test

Cumulative Time Online					
Bed 1 (adsorption rate)		Bed 2 (mass transfer zone)		Bed 3 (breakthrough)	
<i>Sample</i>	<i>Time online (weeks)</i>	<i>Sample</i>	<i>Time online (weeks)</i>	<i>Sample</i>	<i>Time online (weeks)</i>
Q1-1	1.14	All	16.28	3A	4.00
Q2-1	4.00			3B	4.29
Q3-1	8.28			3C	3.86
Q4-1	16.28			3D	1.86
Q1-2*	15.14			3E	2.29
Q2-2*	12.28				
Q3-2*	7.99				

*Indicates replacement quadrant.

Table 2: Sampling protocol for CH₃I adsorption test

Cumulative Time Online					
Bed 1 (adsorption rate)		Bed 2 (mass transfer zone)		Bed 3 (breakthrough)	
<i>Sample</i>	<i>Time online (weeks)</i>	<i>Sample</i>	<i>Time online (weeks)</i>	<i>Sample</i>	<i>Time online (weeks)</i>
Q1-1	0.71	All	13.42	3A	3.43
Q2-1	3.42			3B	4.00
Q3-1	7.71			3C	3.00
Q4-1	13.42			3D	2.43
Q1-2*	12.71			3E	0.57
Q2-2*	9.99				
Q3-2*	5.71				

*Indicates replacement quadrant.

2.4 Sampling Protocol

Sampling events consisted of removal of the sorbent within the selected quadrant or sample bed followed by replacement with fresh sorbent. Upon completion of the test, Bed 2 was removed in discrete sections to allow the progress of the sorbent front through the bed to be determined. Samples were analyzed by neutron activation analysis at Oak Ridge National Laboratory's (ORNL's) High Flux Isotope Reactor to determine iodine content. For the I₂ adsorption test, Quadrants 1-2 and 3-2 are pending analysis at the time of this report's completion.

3. RESULTS

Both the I₂ and CH₃I adsorption tests were completed successfully. The I₂ adsorption test concluded after 16.28 weeks, and the CH₃I adsorption test concluded after 13.42 weeks. The amount of iodine found on the sorbent by neutron activation analysis, along with other associated key data for each sorbent sample, is shown in Table 3 for I₂ adsorption and in Table 4 for CH₃I adsorption.

Table 3: Data obtained by I₂ adsorption test

Sample	Online Time (weeks)	Sample Weight (g)	Iodine collected (mg I/g sorbent) ±
I ₂ -Q1-1	1.14	0.5887	1.58 0.0200
I ₂ -Q2-1	4.00	0.6275	<i>Pending</i>
I ₂ -Q3-1	8.29	0.5810	8.36 0.0400
I ₂ -Q4-1	16.28	0.5958	10.89 0.0600
I ₂ -Q1-2	15.14	0.6307	10.00 0.0500
I ₂ -Q2-2	12.28	0.5755	9.80 0.0600
I ₂ -Q3-2	7.99	0.6087	<i>Pending</i>
I ₂ -Bed2A	16.28	10.8315	0.00 0.0000
I ₂ -Bed2B	16.28	8.5225	3.35 0.0328
I ₂ -Bed2C	16.28	11.4525	<i>Below detection*</i>
I ₂ -Bed2D	16.28	11.7200	<i>Below detection*</i>
I ₂ -Bed2E	16.28	11.5303	<i>Below detection*</i>
I ₂ -Bed2F	16.28	9.9199	<i>Below detection*</i>
I ₂ -Bed2G	16.28	8.8146	<i>Below detection*</i>
I ₂ -Bed2H	16.28	11.3391	<i>Below detection*</i>
I ₂ -Bed3A	4.00	5.0688	<i>Below detection*</i>
I ₂ -Bed3B	4.29	5.0474	<i>Below detection*</i>
I ₂ -Bed3C	3.86	4.9891	<i>Below detection*</i>
I ₂ -Bed3D	1.86	4.9429	<i>Below detection*</i>
I ₂ -Bed3E	2.29	5.1255	<i>Below detection*</i>
<i>*The average minimum detectable activity that was reported for these analyses corresponds to a sorbent loading of 0.0038 mg/I/g sorbent.</i>			

Table 4: Data obtained by CH₃I adsorption test

Sample	Online Time	Sample Weight	Iodine collected	
	(weeks)	(g)	(mg I/g sorbent)	±
CH ₃ I-Q1-1	0.71	0.6433	0.22	0.0030
CH ₃ I-Q2-1	3.42	0.6041	0.34	0.0044
CH ₃ I-Q3-1	7.71	0.6486	3.7	0.0052
CH ₃ I-Q4-1	13.42	0.6094	5.3	0.0064
CH ₃ I-Q1-2	12.70	0.6061	6.3	0.0078
CH ₃ I-Q2-2	9.99	0.6370	6.5	0.0085
CH ₃ I-Q3-2	5.70	0.6286	2.9	0.0057
CH ₃ I-Bed2A	13.42	10.5659	3.2	0.0054
CH ₃ I-Bed2B	13.42	10.7974	0.92	0.0031
CH ₃ I-Bed2C	13.42	9.1888	0.14	0.0021
CH ₃ I-Bed2D	13.42	10.5793	<i>Below detection*</i>	
CH ₃ I-Bed2E	13.42	9.5393	<i>Below detection*</i>	
CH ₃ I-Bed2F	13.42	12.3171	<i>Below detection*</i>	
CH ₃ I-Bed2G	13.42	10.0365	<i>Below detection*</i>	
CH ₃ I-Bed2H	13.42	9.6251	<i>Below detection*</i>	
CH ₃ I-Bed3A	3.42	5.2955	<i>Below detection*</i>	
CH ₃ I-Bed3B	4.00	5.9529	<i>Below detection*</i>	
CH ₃ I-Bed3C	3.00	5.0529	<i>Below detection*</i>	
CH ₃ I-Bed3D	2.42	5.1290	<i>Below detection*</i>	
CH ₃ I-Bed3E	0.57	5.0317	<i>Below detection*</i>	
*The average minimum detectable activity that was reported for these analyses corresponds to a sorbent loading of 0.0039 mg/I/g sorbent.				

3.1 I₂ Adsorption onto Ag⁰Z

The quadrants of Bed 1 were sampled according to Table 1. The iodine loading as a function of time was obtained from the quadrants and is shown in Figure 2. The error bars of the neutron activation analysis are smaller than the data points, but some error may result from analyzing only a portion of the homogenized sample if the homogenization is not fully complete. A more quantifiable estimate of this error is ongoing.

As expected, total adsorbed iodine increases with respect to time over the 16 week test, with the highest iodine loading observed being 11 mg I/g AgZ.

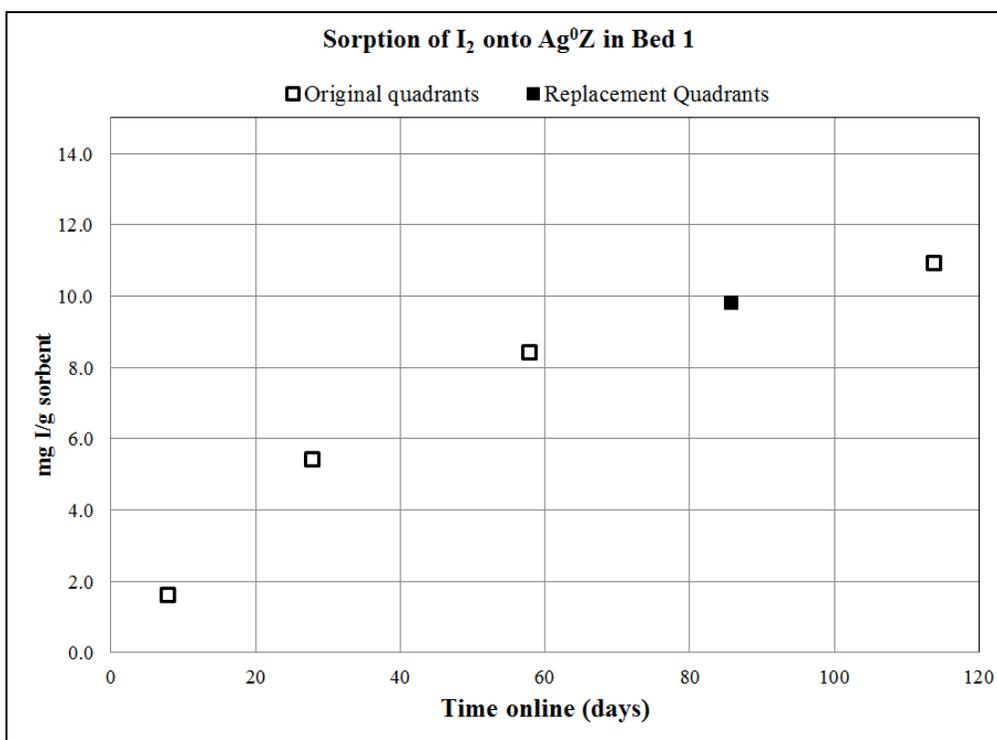


Figure 2: Adsorption of I₂ onto AgZ in bed 1

Bed 2 was removed in sections by vacuum. The sections were each homogenized, and then a small portion was removed for analysis and considered to be the average loading for that section. As shown in Figure 3, I₂ was observed to penetrate 2.2 cm into the sorbent bed. For purposes of this testing, the maximum extent of penetration is defined as the midpoint of the first section containing <1 mg I/g sorbent. This number is 10 times the detection limit of the analytical method. The black bars represent the length of sorbent bed that was removed and homogenized prior to analysis and the average loading of that section. The dotted line is plotted through the midpoint of the section length.

The section length was based upon the density of the as-received material and the weight of each removed section. The density of the material may be altered during testing because the material contacts a humid air stream.

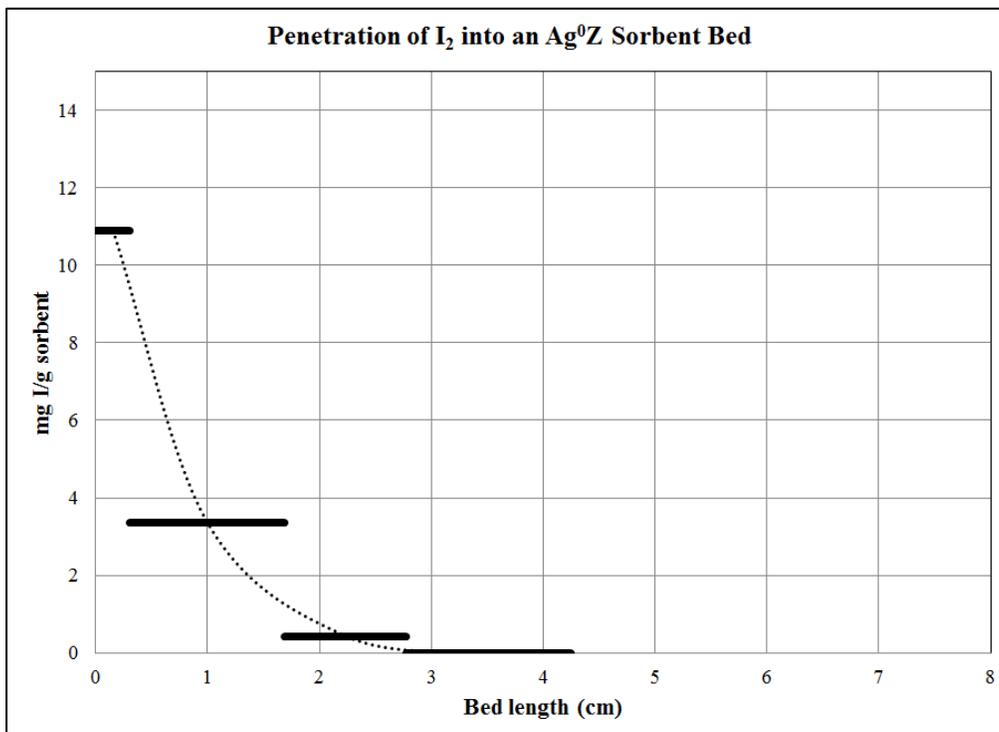


Figure 3: Penetration of I₂ into an AgZ deep bed

The removal of Bed 1 quadrants over the course of the study provided iodine-loaded sorbent material that was online for varying time periods. This allowed the potential effect of sorbent aging to be explored. In Figure 4, the average iodine loading rate is plotted as a function of the time the sorbent bed was online. A decrease in I₂ adsorption rate as a function of sorbent time online was observed for this study.

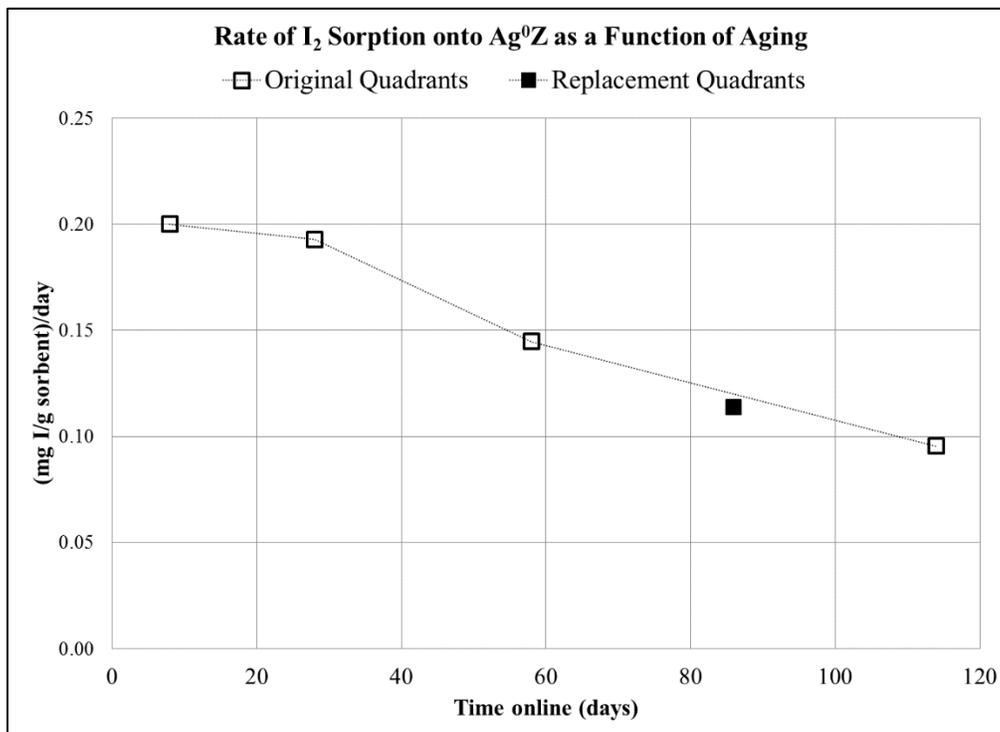


Figure 4: Rate of I₂ sorption onto Ag⁰Z as a function of aging

As a check of the system, the total amount of iodine recovered from the sorbent bed was compared to the intended delivery amount. The amount of iodine recovered on the beds was approximately 85% of the amount that was expected to be delivered.

3.2 CH₃I Adsorption onto Ag⁰Z

The quadrants of Bed 1 were sampled according to Table 2 by the method described in Section 3.1. The iodine loading as a function of time was obtained from the quadrants and is shown in Figure 5. Total adsorbed iodine increases with respect to time over the 13 week test to a maximum iodine loading of 6 mg I/g AgZ. CH₃I was observed to penetrate 2.4 cm into the sorbent bed (Figure 6). As shown in Figure 7, no trend was observed with respect to the rate of CH₃I adsorption as a function of sorbent time online. The amount of iodine recovered on the sorbent beds was only 33% of the amount expected to be delivered. This type of discrepancy between CH₃I delivery and recovery has been observed in previous testing and efforts are underway to identify the cause (Bruffey et al. 2016).

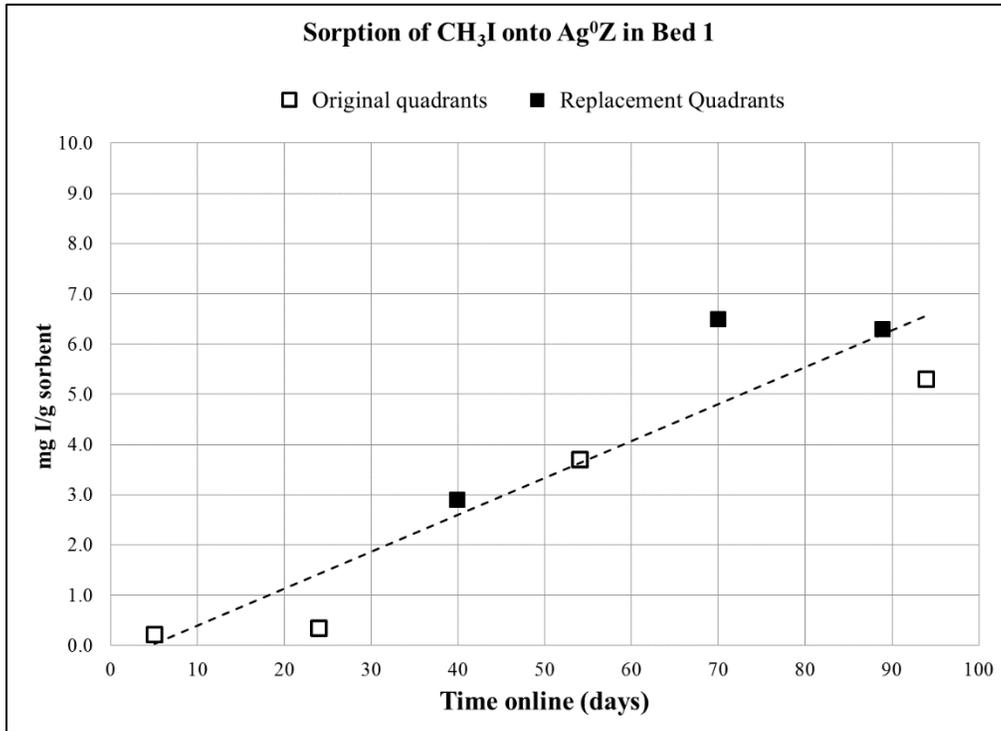


Figure 5: Adsorption of CH₃I onto AgZ bed 1

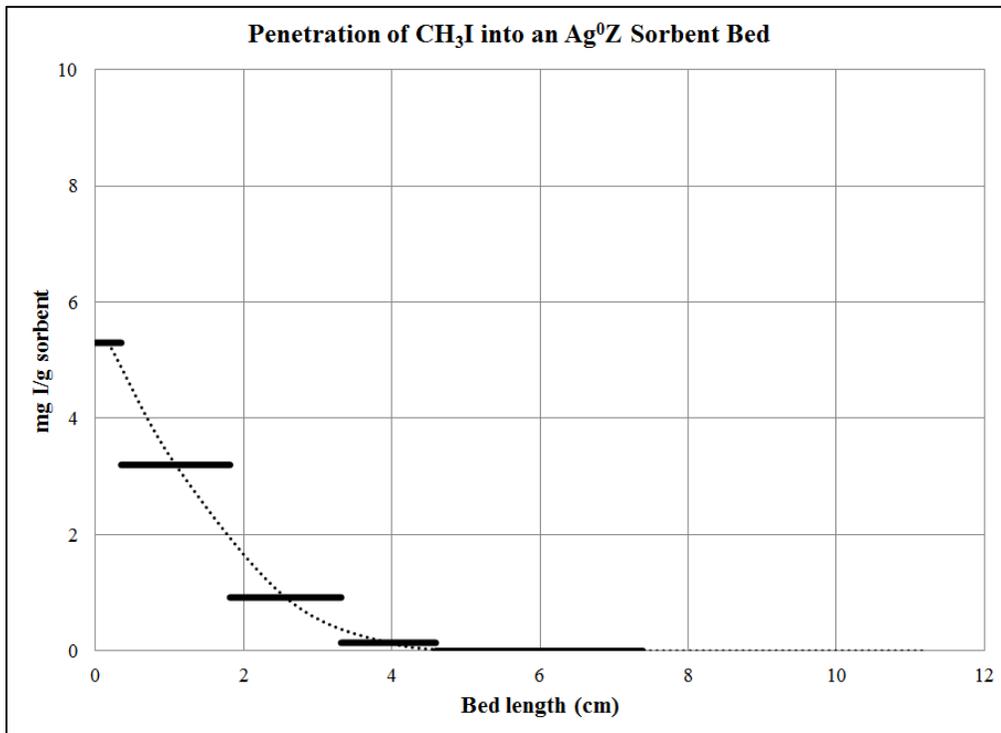


Figure 6: Penetration of CH₃I into an AgZ deep bed

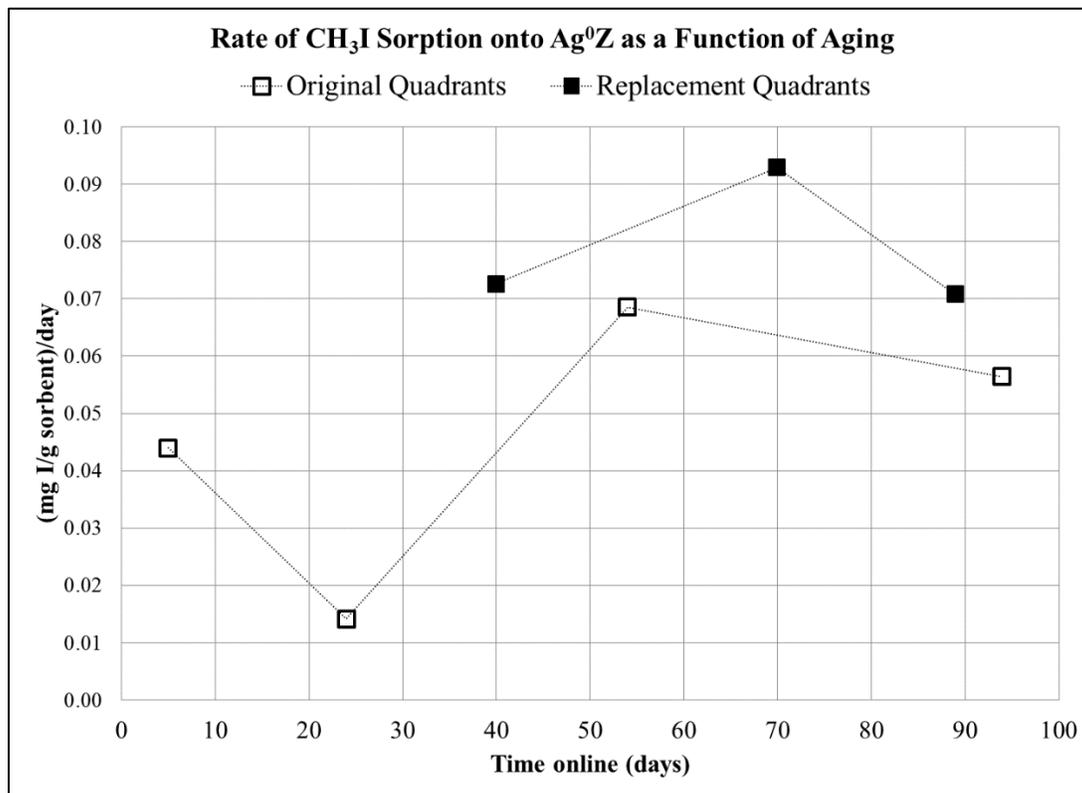


Figure 7: Rate of CH₃I sorption onto Ag⁰Z as a function of aging

4. DISCUSSION

4.1 Comparison of I₂ and CH₃I Adsorption onto AgZ

Direct comparisons between the results of the I₂ and CH₃I adsorption testing are not possible as the tests were conducted at different total iodine concentrations. However, some qualitative inferences can be made. Elemental iodine penetrated the sorbent bed to a depth of 2.2 cm. CH₃I only penetrated to a depth of 2.4 cm, despite CH₃I being more concentrated in the inlet gas stream. However, I₂ in Bed 1 adsorbed to a total loading twice that of CH₃I in Bed 1 (11 mg I/g sorbent and 6 mg I/g sorbent, respectively). Figure 8 represents the percentage of iodine adsorbed by AgZ for each species as a function of bed depth. Although this representation may be affected by the open mass balance for the CH₃I test, it is observed that all of the I₂ recovered was found within the first 2 cm of the bed. The amount of CH₃I recovered was distributed over 3 cm. It will not be possible to confirm or disprove the penetrating nature of CH₃I until the mass balance can be closed, as one potential explanation for the open mass balance is that CH₃I passes through the sorbent bed entirely.

The rate of uptake for the two species was found to vary by a factor of two, as shown in Figures 4 and 7. Elemental iodine, even at lower concentrations, was found to be adsorbed twice as quickly as CH₃I.

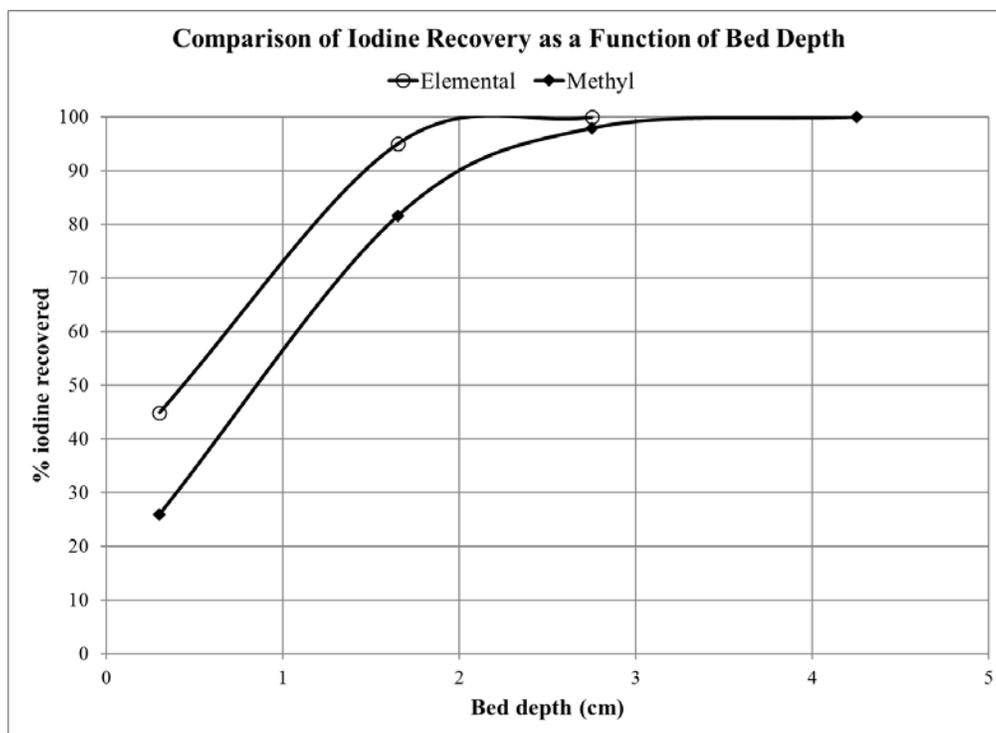


Figure 8: Comparison of iodine recovery as a function of bed depth

When examining the effects of aging, it was found that the rate of I_2 adsorption appeared to decrease as a function of time online (Figure 4). This supports the existence of an aging effect for I_2 adsorption from AgZ. In contrast, no sorbent aging effects were observed for the CH_3I adsorption testing.

4.2 Decontamination Factor

4.2.1 Estimation Method

Periodic removal and replacement of Bed 3 as detailed in Table 1 was intended to detect breakthrough of Bed 2 and allow the subsequent calculation of the DF. There is one key assumption in this approach—the sorbent in Bed 3 is effective at concentrations well below the feed concentration, thus adsorbing all (or at least measurable amounts of) iodine contacting it.

Equation 1 is used to calculate the concentration in the gas stream exiting Bed 2. Some extent of breakthrough is required to be measured to avoid division by zero in the calculation of the DF by Equation 2.

$$[CH_3I]_{Bed\ 2\ outlet} = \frac{g\ I\ recovered\ per\ Bed\ 3\ sample}{Gas\ flow\ rate \times sample\ time\ online} \quad (\text{Equation 1})$$

$$Decontamination\ Factor = \frac{[CH_3I]_{in}}{[CH_3I]_{out}} \quad (\text{Equation 2})$$

4.2.2 Estimation of Iodine Removal

No iodine was observed in Bed 3 above the detection limit for NAA for either I_2 or CH_3I adsorption testing. Thus, the DF for this system cannot be calculated. The level of detection for the neutron activation analysis (NAA) analysis of these samples was 0.037 mg I/g sorbent. Thus, assuming all of the

I₂ passing through Bed 2 is subsequently trapped on Bed 3 and using the Bed 3 sample size of 5 g with an online time of four weeks, the concentration of the I₂ exiting Bed 2 is calculated to be 145 parts-per-trillion (ppt). Based on the intended feed concentrations of 40 ppb, the resulting estimated DF based on Eqn. 2 is 275. This value is thought to be below the actual DF and is an artifact of the approach used and is limited by (1) the detection limit for NAA and (2) the time the sample was online. If the time online had been greater for the Bed 3 samples, the calculated exit concentration would be reduced per Eqn. 1. In a like manner, the calculated exit concentration would also be reduced if the detection limit was lower.

While the samples in Bed 3 were periodically replaced, all of Bed 2 was online for the entire run duration of 13.42 weeks. The loading on Bed 1 and on the first several centimeters of Bed 2 represents the leading edge of the mass transfer zone. If the final portion of Bed 2, with a mass of 11 g, is considered as a sampler for the amount of I₂ leaving the mass transfer zone of the bed, then applying Eqn. 1 yields a value of 80 ppt in the effluent using the assumptions previously detailed, and the resultant estimated DF is 501.

If the same treatment is applied to the results of the CH₃I adsorption testing, the DF using Bed 3a as a sampler is then estimated as 217, and the DF using Bed 2h as a sampler is estimated as 466.

4.2.3 Critical Assumptions

This type of approach should be considered as solely an estimation method. A DF can only be accurately calculated when the specie of interest breaks through the bed at detectable levels. However, due to the dilute concentration of iodine required to simulate VOG conditions, breakthrough of even small sorbent beds such as these could require experiments to be online longer than one year. The DF estimation provided here is an attempt to characterize the performance of AgZ in removing I₂ and CH₃I from a dilute gas stream, but is limited by the detection limit of the analysis, the mass of the sorbent bed, and the time online. It also makes the assumption that the sorbent effectively removes all iodine in the effluent even in very dilute streams, which is an assumption that has not yet been verified.

4.3 Observations and Conclusions

There are outstanding questions concerning the aging of the sorbent bed in any off-gas system, but especially in a vessel off-gas system. Aging of a sorbent for extended periods of time in a flowing gas stream is known to result in a decrease in iodine capacity for sorbents (Bruffey et al. 2015b). However, the capacity of the aged sorbent has typically been measured through exposure of the sorbent to prototypical DOG streams containing ppm levels of iodine; the iodine capacity of aged material in very dilute iodine-containing streams has not been studied. Additionally, aging studies have been limited to the adsorption of elemental iodine (I₂); extension of this work to evaluate impacts of aging on CH₃I adsorption has not been performed. Finally, it is difficult to elucidate whether a decrease in iodine uptake over time reflects an approach to the unknown saturation level of the aged sorbent or whether aging also affects the kinetics of iodine adsorption. Future experiments should examine methods to resolve these knowledge gaps. In light of these results, research should especially seek to elucidate any differences that could be observed with regard to aging for different iodine species.

The mass balance for iodine within the CH₃I adsorption system was unable to be closed, with only 33% of iodine delivered subsequently found on the sorbent beds. The following are offered as potential causes. First, the amount of iodine successfully delivered to the system could have been less than expected due to CH₃I holdup within the feed system or other feed system problems. Second, the samples are removed from the system by vacuum. Although chemisorbed iodine will not be affected by this process, any iodine that is only physisorbed or perhaps not sorbed at all, could have been lost during this vacuum operation. Finally, it is possible that AgZ is unable to remove CH₃I from an extremely dilute gas stream, which would result in iodine passing through the bed undetected by the methods used for this study.

Future efforts on the adsorption of iodine from prototypical vessel off-gas streams by silver-based sorbents will attempt to resolve some of the questions raised here, both regarding the mass balance of CH_3I and the effect of aging on iodine adsorption by AgZ from a dilute gas stream. Additionally, the adsorption of different iodine species, such as $\text{C}_{12}\text{H}_{25}\text{I}$, will be studied. Other variables that merit examination are the gas velocity of the test and the dependence of the observed results on the inlet iodine concentration. Finally, longer duration testing or modified test methods should be considered in an effort to determine the mass transfer zone and DF associated with iodine adsorption by AgZ under prototypical vessel off-gas conditions.

5. REFERENCES

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