# *Extended Elemental Iodine Adsorption by AgZ under Prototypical Vessel Off-Gas Conditions*

## Nuclear Technology Research and Development

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# SUMMARY

US 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 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 (WOG), and the shear off-gas (SOG). To achieve regulatory compliance, treatment of multiple off-gas streams within the plant must be performed. Of these remaining streams, the VOG is expected to be one of the major contributors to the balance of the residual iodine releases. The VOG will most likely contain iodine at parts-per-billion (ppb*) concentrations.

Preliminary studies were completed on the adsorption of $I_2$ onto hydrogen-reduced silver mordenite ($Ag^0Z$) from prototypical VOG streams. The previous tests were of relatively short duration (3–4 months) and loaded the sorbent to far less than its expected saturation loading. As a result, little to no information could be extracted regarding the length of the mass transfer zone or the long-term concurrent sorbent aging and loading behavior. The test reported here is the first part of a series of long-duration tests designed to identify the saturation loading of the sorbent under VOG conditions and, as a part of this, to determine the length of the mass transfer zone.

This test represents the longest extended VOG test conducted to date by this program. This test ran 38 weeks and achieved iodine loadings of ~40 mg I/g sorbent. The iodine mass transfer zone penetrated at least 10.5 cm into the sorbent beds. There was no indication of sorbent saturation. The mass balance for iodine closed within 2%, which is within the expected combined uncertainty.

While this test did not achieve saturation of any portion of the test beds, the data does provide significant information that can be used to extrapolate a potential maximum length of the mass transfer zone under VOG conditions. Under the conditions used in this test, the mass transfer zone could be on the order of 21 cm.

This test also provides the basis for the design of the next series of extended VOG tests. Future tests to examine the validity of the extrapolation to a saturated VOG sorbent bed should be designed to run up to ~4.9 years, assuming a 50 ppb $I_2$ feed gas, and have a bed length greater than 32 cm.

Future efforts regarding the adsorption of iodine from prototypical VOG streams by silver-based sorbents will attempt to extend the test duration to (1) determine if the slope of the iodine loading front remains constant; (2) determine the saturation concentration reflecting aging in situ; and (3) compare the extended loading behavior for organic iodides. Additionally, the adsorption of different iodine species, such as $C_{12}H_{25}I$, 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.

* Throughout this report, ppb or ppm concentrations will be used on a molar basis.

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# ACRONYMS

| | |
|---|---|
| AgZ | Silver mordenite |
| $Ag^0Z$ | Reduced silver mordenite |
| COG | Cell off-gas |
| DF | Decontamination factor |
| DOG | Dissolver off-gas |
| NAA | Neutron activation analysis |
| SOG | Shear off-gas |
| UNF | Used nuclear fuel |
| VOG | Vessel off-gas |
| WOG | Waste off-gas |

# EXTENDED ELEMENTAL IODINE ADSORPTION BY AgZ UNDER PROTOTYPICAL VESSEL OFF-GAS CONDITIONS

## 1. INTRODUCTION

US 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 ($^{3}H$, $^{14}C$, $^{85}Kr$, 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 et al. 2012).

Multiple off-gas streams are generated within a UNF reprocessing plant, and the total from all of these streams must be considered when assessing the environmental release since each 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 (WOG), and the shear off-gas (SOG). While 95–98% of the total iodine inventory of UNF is expected to be released to the DOG, even complete removal of iodine from the DOG without treatment of other streams would result in an overall plant DF of <100 (Jubin et al. 2013). Thus, to achieve regulatory compliance, treatment of multiple off-gas streams within the plant must be performed.

Of these remaining streams, the VOG is expected to be one of the major contributors to the balance of the residual iodine releases. The VOG will most likely contain iodine at parts-per-billion (ppb*) concentrations. Vessel off-gas refers to the gas venting from 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. Volatile components and their degradation products present in the solvent extraction vessels can transfer to these gas streams and/or react with the iodine present in liquid or gas phases. The VOG will most likely contain iodine at ppb concentrations. The VOG is also the stream most likely to contain organic iodides, which have been considered more difficult to remove (or more *penetrating*) than $I_2$ when using with traditional sorbents (Bruffey et al. 2015a).

Silver-exchanged mordenite (AgZ) has been considered a promising iodine sorbent for use in UNF reprocessing plants, but recent efforts have identified silver-functionalized silica-aerogel (AgAerogel) as an alternative iodine sorbent. In testing under simulated DOG stream conditions, AgAerogel demonstrates a resistance to degradation from $NO_x$ gases present within the plant, has high iodine loadings by weight, and is easily converted to a condensed waste form through hot isostatic pressing (Bruffey et al. 2015b; Matyas et al. 2016). However, the mechanism for iodine adsorption and immobilization by AgAerogel is not yet understood, and it is not currently available in an engineered form with a large particle size and resistance to mechanical and thermal degradation.

Several years ago, Oak Ridge National Laboratory initiated an effort to evaluate both hydrogen-reduced AgZ ($Ag^0Z$) and AgAerogel under simulated VOG conditions. Initial tests were performed to evaluate the adsorption of elemental and organic iodine (Jubin et al. 2015; Bruffey et al. 2016). These tests were typically 3–4 months in duration because at the low iodine concentrations in the prototypical VOG stream, considerable time was required to even begin to achieve significant iodine loading on the sorbent materials as compared to loading with prototypic DOG streams. These efforts were continued in 2017 and

* Throughout this report, ppb or ppm concentrations will be used on a molar basis.

characterized the adsorption of 7 ppb $I_2$ by $Ag^0Z$, 40 ppb methyl iodide ($CH_3I$) by $Ag^0Z$, and 40 ppb $CH_3I$ by AgAerogel (Jubin, et al. 2017).

The previous tests were of relatively short duration (3–4 months) and loaded the sorbent to far less than its expected saturation loading. As a result, little to no information could be extracted regarding the length of the mass transfer zone or the long-term concurrent sorbent aging and loading behavior. The test reported here is the first part of a series of long-duration tests designed to identify the saturation loading of the sorbent under VOG conditions and, as a part of this, to determine the length of the mass transfer zone.

# 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 9.4 wt% silver and has a 0.16 cm pellet diameter. Prior to 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).

Due to the corrosive nature of iodine, 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 = 2.73 cm) and separated by glass frits. The test bed system consisted of three separate deep beds in series, as shown in Figure 1. The glass connections between the beds were built to allow a slipstream to be pulled between beds. These were used to qualitatively verify that flow was passing through the bed.

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. Each glass column was filled with ~90 g of mordenite, resulting in a bed depth of 17.35 cm. each.

## 2.2 Test Conditions

For this $I_2$ adsorption test, the iodine stream was generated by a KinTek Flexstream Gas Standards Generator. Testing lasted from 31 May 2017 to 23 February 2018, for a total of 268 days online. During the first 127 days of testing, three permeation tubes were used in the KinTek with a combined emission rate of 1866 ng/min. During the second phase of the test (141 days), a single permeation tube with an emission rate of 2097 ng/min was used. The concentrated iodine stream from the KinTek was combined with a humidified air stream such that the resulting feed gas stream provided a face velocity of ~10 m/min (based on the empty column diameter), a 0°C dew point, and elemental iodine concentration of ~50 ppb.

The sorbent beds were held at 150°C, and the gas stream was preheated to 150°C prior to contact with the sorbent beds.

## 2.3 Testing Protocol

The test system was left in the oven at operating temperature for the duration of the test period. Throughout the course of the test, minor feed gas outages occurred as a result of system maintenance operations (such as refilling of the humidity generator). During the course of this test, no sampling of the individual beds was conducted to avoid disturbing the iodine loading profile.

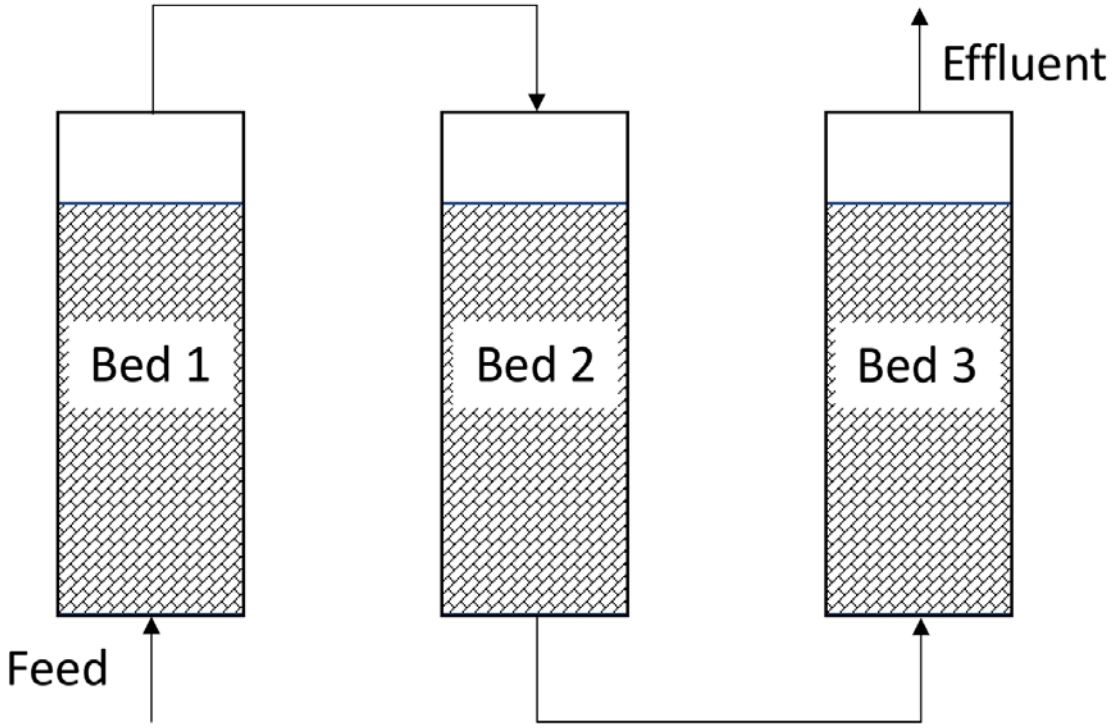


Figure 1. Schematic of test system.

## 2.4 Sampling Protocol

At the end of the test period, the individual beds were sampled by vacuuming and collecting discrete portions beginning at the top of each bed. The sections were nominally 1 cm. in length in the first bed and 1.25 cm in the second and third beds. The segments recovered from the first bed had an average weight of 5.75 g. Each of these bed segments was individually mixed by hand in glass containers. A small sub-sample of roughly 0.2 g was taken from each of the segments from the first bed and sent for neutron activation analysis (NAA) at ORNL's High Flux Isotope Reactor to determine iodine content.

# 3. RESULTS AND DISCUSSION

The $I_2$ adsorption test was completed successfully. The $I_2$ adsorption test concluded after 38 weeks. The amount of iodine found on the sorbent by NAA, along with other associated key data for each sorbent sample, is shown in Table 1. As iodine was not expected to penetrate into the second and third sorbent beds, only selected segments from the first bed were analyzed. The first 10 segments of the first sorbent bed displayed measurable iodine loading.

Table 1. Data obtained for Bed 1 of extended $I_2$ adsorption test #1

| Sample | Sample Weight | Segment Length | Cummulative Length | Iodine Collected | NAA Uncertainty |
|---|---|---|---|---|---|
| | (g) | (cm) | (cm) | (mg I/g sorbent) | (± mg I/g sorbent) |
| Section 1 | 6.2587 | 1.21 | 1.21 | 38.8399 | 0.5684 |
| Section 2 | 8.0743 | 1.56 | 2.76 | 32.2192 | 0.4680 |
| Section 3 | 6.3494 | 0.65 | 3.41 | 21.3214 | 0.3204 |
| Section 4 | 6.6753 | 1.29 | 4.69 | 15.7153 | 0.2372 |
| Section 5 | 5.361 | 1.03 | 5.73 | 11.7351 | 0.1831 |
| Section 6 | 5.3931 | 1.04 | 6.77 | 4.6500 | 0.0763 |
| Section 7 | 6.5487 | 1.26 | 8.03 | 2.5852 | 0.0459 |
| Section 8 | 6.4116 | 1.24 | 9.27 | 0.6815 | 0.0172 |
| Section 9 | 4.6104 | 0.89 | 10.12 | 0.1649 | 0.0100 |
| Section 10 | 4.0461 | 0.78 | 10.93 | 0.0075 | 0.0071 |
| Section 11 | 6.6901 | 1.29 | 12.22 | MDA* | |
| Section 12 | 5.7895 | 1.12 | 13.34 | MDA* | |
| Section 13 | 4.4243 | 0.85 | 14.19 | MDA* | |
| Section 14 | 5.8134 | 1.12 | 15.31 | MDA* | |
| Section 29 | 6.5295 | 1.26 | 16.57 | MDA* | |
| Section 30 | 5.4074 | 1.04 | 17.61 | MDA* | |
| Section 31 | 3.626 | 0.70 | 18.31 | MDA* | |
| **MDA = below minimum detectable activity* | | | | | |

## 3.1 $I_2$ Adsorption onto $Ag^0Z$

As noted above, the three beds were removed in sections/layers by vacuum. The sections were each homogenized, and then, in the case of Bed 1, a small portion was removed for analysis and considered to be the average loading for that section. The results from the NAA are presented in Table 1 and graphically shown in Figure 2. The black bars in Figure 2 represent the length of sorbent bed that was removed and homogenized prior to analysis and are plotted to show 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, 0.886 g/cm$^3$, and the weight of each removed section. The density of the material may be altered during testing as the material contacts a humid air stream.

The vertical lines through the midpoint of each segment bar in Figure 2 represent the error band for that data point. This error band is composed of two parts; the first part is the uncertainty associated with the NAA analysis (this is shown in Table 1), and the second part is an estimate of the variable of a single 0.2 g sub-sample from the larger 5–8 g sample. This variability was previously determined to be ~12%–27% for subsamples that represented 2%–3% of a large deep bed and ~10% for subsamples that represent significantly larger fractions of thin beds (Jubin et al. 2017). For this estimation of sampling variance, the value of 10% was selected.

As a check of the system, the total amount of iodine recovered from the sorbent bed was compared to the intended delivery amount based on the permeation rates. The amount of iodine recovered on the beds was approximately 102% of the amount that was expected to be delivered. This is within the combined error band.

As shown in Figure 2, the iodine mass transfer zone penetrated approximately 10.5 cm into Bed 1. For purposes of this test, the maximum extent of penetration was defined as the midpoint of the first section containing <0.1 mg I/g sorbent. There was also no indication of saturation loading at the bed inlet. The iodine loadings on the first and second bed segments of Bed 1 (each ~1 cm in depth) were 38.8 mg $I_2$/g sorbent and 32.2 mg $I_2$/g sorbent, respectively. It was also noted that over the first 6–6.5 cm the iodine loading appeared to be linear or nearly linear as a function of bed depth.

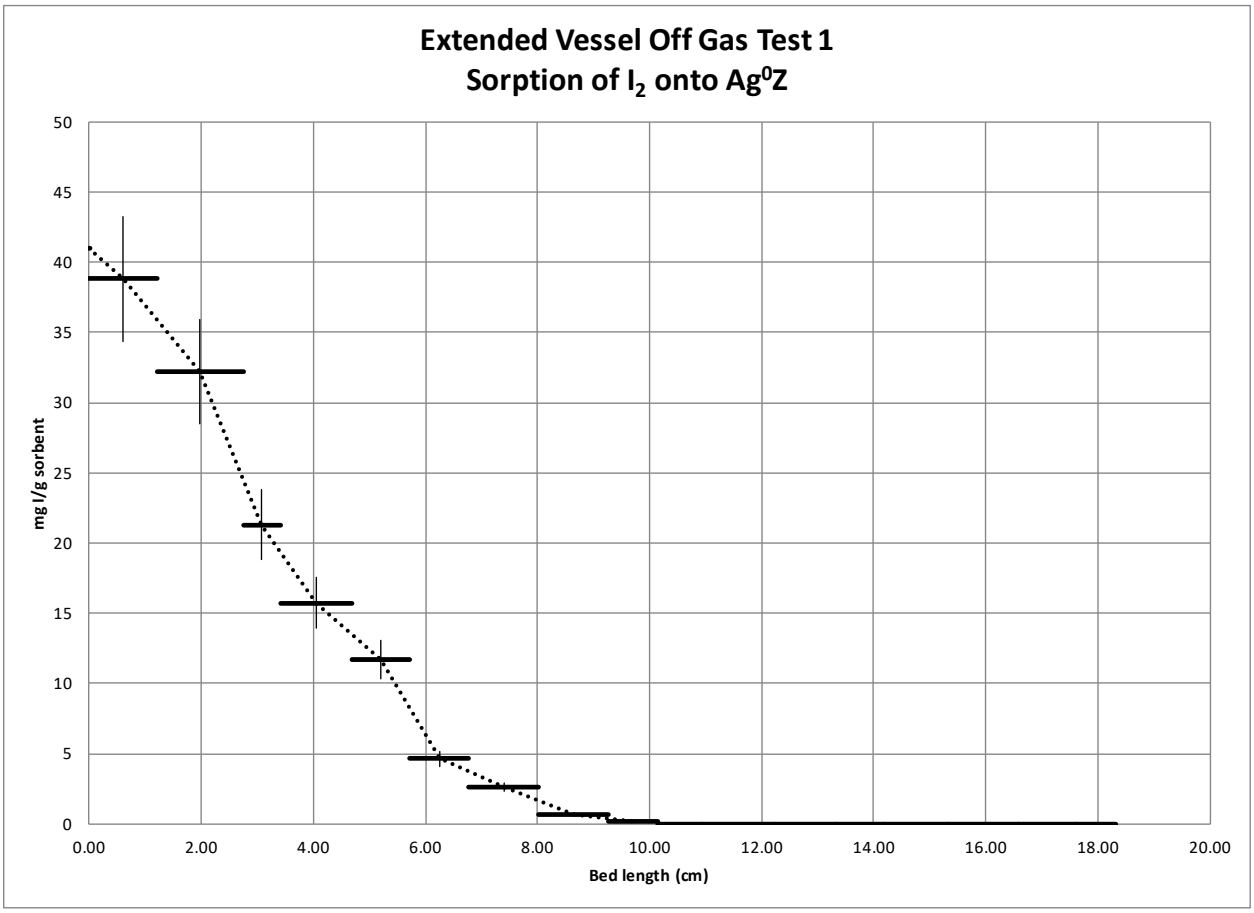


Figure 2. Penetration of $I_2$ into Bed 1 of the test system.

Figure 3 shows this same data with a linear regression fit for the initial bed segments. The resulting equation is

$$y = mx + b,$$

where

$y$ = mg I / gm sorbent,
$x$ = penetration depth (cm),
$m$ = -6.122 mg I / gm sorbent / cm, and
$b$ = 42.361 mg I / gm sorbent.

The coefficient of correlation ($R^2$) is 0.983.

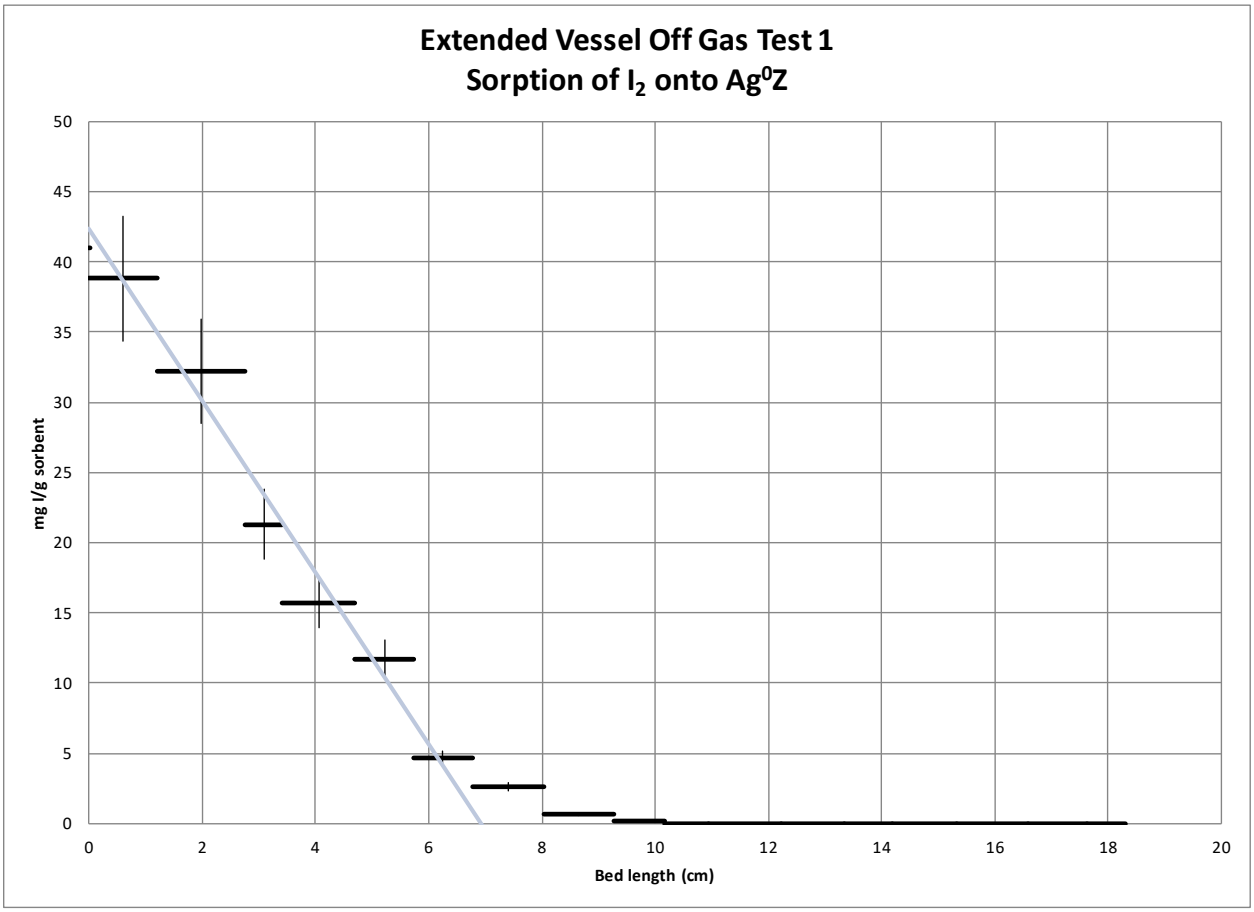


Figure 3. Linear regression fit for the mass transfer zone for the extended $I_2$ sorption onto $Ag^0Z$.

It is clear from Figure 2 that the inlet had not yet reached saturation, and as a result the length of the mass transfer zone could not be determined from this test data. However, assuming that the linear relationship shown in Figure 3 continues with the same slope as the bed loading continues, an estimate of the time to reach a specified level of saturation can be made. Figure 4 represents such an estimate. In this case, a saturation loading goal of 90 mg $I_2$/g sorbent is specified, corresponding to a silver utilization of 80%. This is believed to be a very conservative value considering the aging of the sorbent that would occur during the course of the test based on previous studies by Jubin (2011) that examined the effect of

extended aging at 150°C with both dry and humid streams for periods up to 6 months prior to iodine loading. These tests showed a 40% capacity loss for a 6 month exposure to dry streams and 60% loss for a 4 month exposure to a humid air stream. Symmetry is also assumed in the shape of the loading curve in Figure 4 (i.e., an "S"-shaped loading curve). Based on the slope of the loading curve, the length of the mass transfer zone is estimated to be approximately 21 cm. The total iodine loaded into the mass transfer zone and very short tails is ~5.6 g on the 126 g of sorbent. Based on the loading and the same 50 ppb $I_2$ feed gas used in this test, it would require a minimum test duration of ~254 weeks.

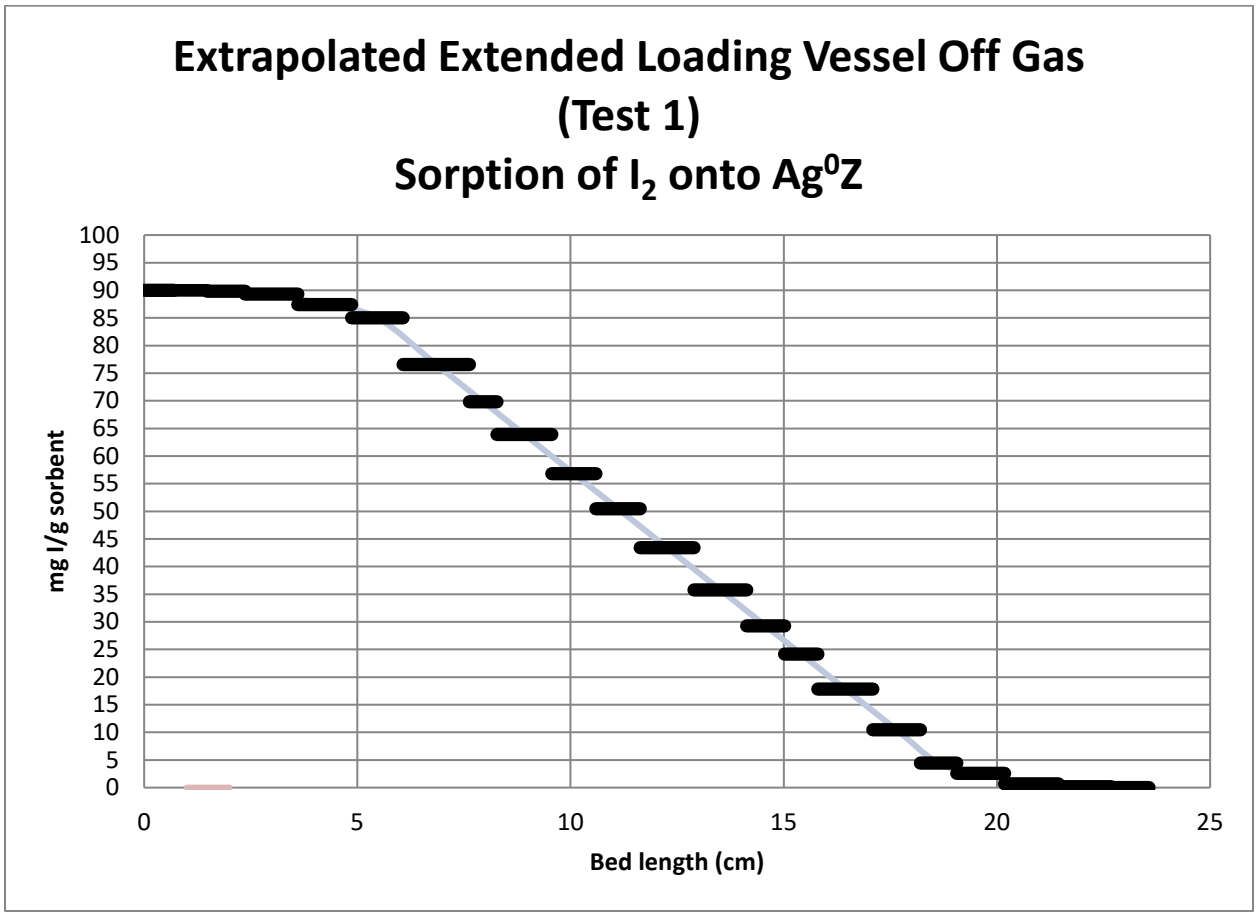


Figure 4. Estimated penetration of $I_2$ into an $Ag^0Z$ deep bed at breakthrough based on linear regression fit of loading shown in Figure 3 with a saturation loading of 90 mg $I_2$/g sorbent.

Figure 5 represents a lower estimate of a saturation load representing the 60% loss of capacity. In this case, a saturation loading is assumed to be 45 mg $I_2$/g sorbent. This is also seems reasonable based on the maximum loading achieved (~40 mg $I_2$/g sorbent) prior to the termination of this extended test. The same symmetry is also assumed in the shape of the loading curve in Figure 4 (i.e., an "S"-shaped loading curve). This iodine load scenario assumes the same duration (~254 weeks with a 50 ppb $I_2$ feed gas) as determined in the previous estimate as represents the same total amount of iodine captured on the bed accounting for the lower saturation loading. Based on the slope of the loading curve, the length of the mass transfer zone is estimated to be approximately 13 cm. The total iodine loaded into the mass transfer zone and very short tails is ~5.6 g on the 171 g of sorbent. The minimum bed length required in this case is ~32 cm as compared to ~24 cm in the higher saturation loading case shown in Figure 4.

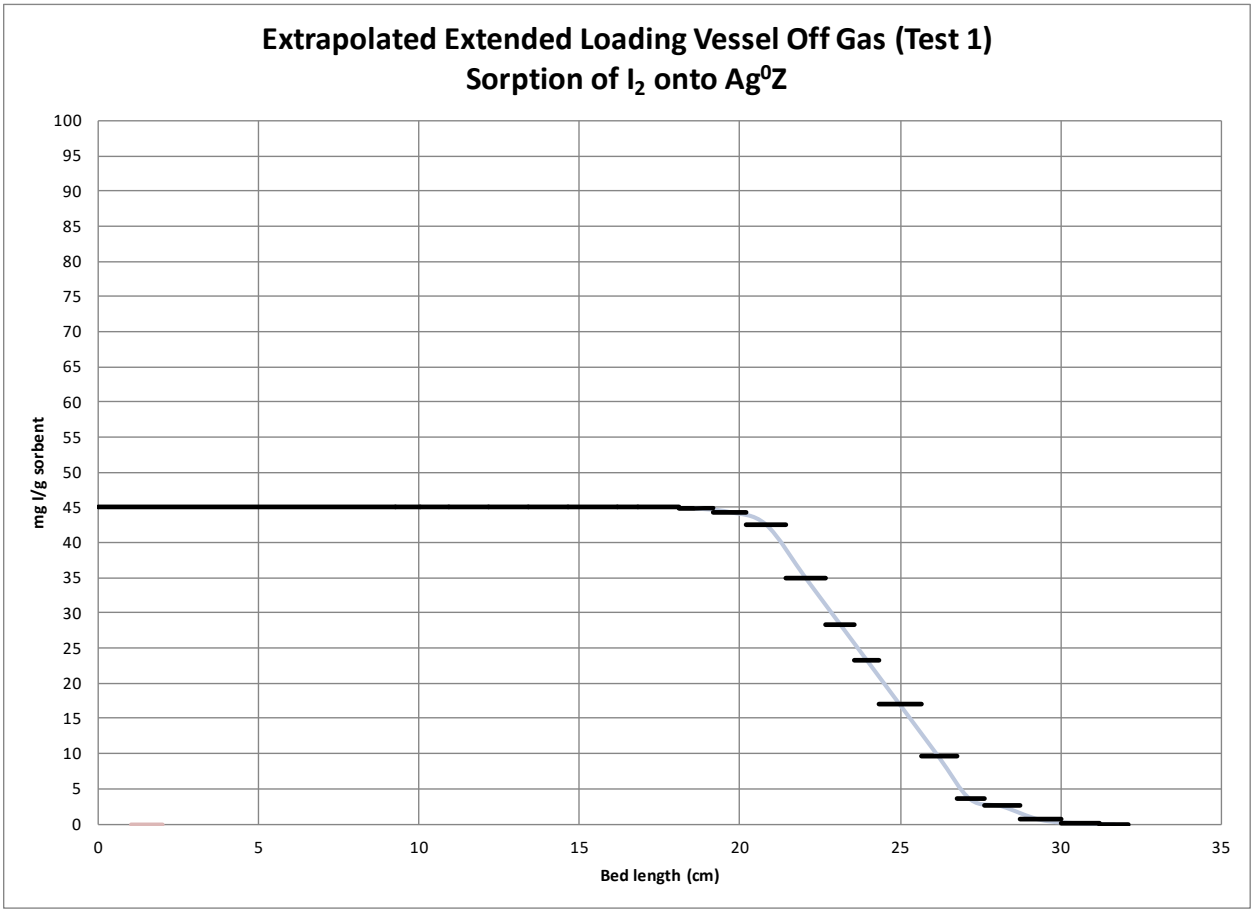


Figure 5. Estimated penetration of $I_2$ into an $Ag^0Z$ deep bed at breakthrough based on linear regression fit of loading shown in Figure 3 with a saturation loading of 45 mg $I_2$/g sorbent.

## 3.2 Observations and Conclusions

This test represents the longest extended VOG test conducted to date by this program. This test ran 38 weeks and achieved iodine loadings of ~40 mg $I_2$/g sorbent. The iodine mass transfer zone penetrated at least 10.5 cm into the sorbent beds. Over the first 6–6.5 cm of the bed, the iodine loading in mg I / gm sorbent appeared to be linear or nearly linear as a function of bed depth. There was no indication of sorbent saturation. The mass balance for iodine closed within 2%, which is well within the expected combined uncertainty.

While this test did not achieve saturation of any portion of the test beds, the data does provide significant information that can be used to extrapolate a potential maximum length of the mass transfer zone under VOG conditions. Under the conditions used in this test, the mass transfer zone could be on the order of 21 cm.

This test also provides the basis for the design of the next series of extended VOG tests. Future tests to examine the validity of the extrapolation to a saturated VOG sorbent bed should be designed to run up to ~4.9 years, assuming a 50 ppb $I_2$ feed gas and have a bed length greater than 32 cm.

Future efforts on the adsorption of iodine from prototypical VOG 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 $Ag^0Z$ from a dilute gas stream. Additionally, the adsorption of different iodine species, such as $C_{12}H_{25}I$, 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. An assessment of the residual iodine capacity of the sorbent media following the 8-month online time using media from the final bed segments should also be completed. 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 $Ag^0Z$ under prototypical vessel off-gas conditions.

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