Analysis of Organoiodide Adsorption Mechanisms

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SUMMARY

If the United States were to engage in the reprocessing of used nuclear fuel, radioactive iodine must be removed from multiple plant off-gas streams to comply with governing regulations. One of these streams is the vessel off-gas (VOG), which arises from the separations process and is expected to contain iodine in primarily organic iodine forms and at parts-per-billion concentrations. The relative lack of knowledge surrounding organic iodine removal from the VOG prompted the US Department of Energy's Office of Nuclear Energy to initiate experimental efforts targeted at understanding organic iodide removal from prototypic VOG streams. At Oak Ridge National Laboratory (ORNL), this effort has focused on developing a comprehensive understanding of iodine removal from VOG streams by using silver-based sorbents. An important aspect of this testing is developing an understanding of how the sorption of methyl iodide (CH_3I), the most studied organic iodide species to date, compares with the sorption of other volatile organic iodide species potentially present in the VOG.

The work presented here reflects initial testing that will continue to be developed, and final results will be incorporated into an end-of-year report that details a multiyear testing campaign designed to understand iodine mitigation from VOG streams. The goal of these experiments was to determine whether similar reaction pathways govern both CH_3I and iodobutane (C_4H_9I) sorption onto silver mordenite (AgZ), a common silver-based iodine sorbent. More specifically, the authors hypothesized that the sorption of C_4H_9I by AgZ will result in the formation of butanol (C_4H_9OH). Effluent monitoring of CH_3I sorption testing has confirmed methanol production, but analogous monitoring of effluents from C_4H_9I sorption studies has not been performed.

A series of tests was completed to test this hypothesis with the aim of detecting C_4H_9OH downstream of the AgZ bed. Test conditions varied the bed depth, gas stream humidity, and bed temperature post sorption. The effluent gas stream downstream of the AgZ bed was sampled by using gas-tight syringes, and these samples were analyzed by a gas chromatograph coupled to a mass spectrometer.

Thin bed C_4H_9I tests conducted at -65 and 0°C dew points did not result in C_4H_9OH detection in the effluent. This suggests that the sorption mechanism and subsequent reactions could be different from those observed for CH_3I. The sorption testing continues; additional results will be included in final end-of-year report and will increase the fundamental understanding of organic iodide sorption by AgZ from VOG streams.

CONTENTS

FIGURES

TABLES

ACRONYMS

AgI	silver iodide
AgZ	silver mordenite
BDL	below limit of detection
BQL	below limit of quantification
C_2H_6	ethane
CH_3I	methyl iodide
CH_3OH	methanol
C_4H_9I	iodobutane
C_4H_9OH	butanol
$C_{12}H_{25}I$	iodododecane
DF	decontamination factor
DME	DME
DOG	dissolver off-gas
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
I_2	elemental iodine
INL	Idaho National Laboratory
LOD	limit of detection
LOQ	limit of quantification
MS	mass spectrometer
ORNL	Oak Ridge National Laboratory
SPME	solid phase microextraction
TGA	thermogravimetric analyzer
VOG	vessel off-gas

ANALYSIS OF ORGANOIODIDE ADSORPTION MECHANISMS

1. INTRODUCTION

The aqueous reprocessing of used nuclear fuel releases four key volatile radionuclides—^{3}H, ^{14}C, ^{85}Kr, and ^{129}I—from the used fuel into the off-gas streams of a reprocessing facility. Off-gas streams, which typically converge to one environmental discharge point, are treated within the facility to remove volatile radionuclides. Analysis shows that of these four volatile elements, iodine will require the highest level of removal to comply with US Environmental Protection Agency regulations (Jubin et al. 2012). An evaluation was conducted that assessed the practical impact of these regulations, and it found that an overall plant decontamination factor (DF)[a] of 1,000 is likely the minimum required iodine abatement efficiency (Jubin et al. 2017). Depending on the specifics of the reprocessing facility and reprocessed fuel, the required DF could be as high as 8,000.

Iodine is released during multiple unit operations within the plant and can be found in gas streams such as the shear off-gas, dissolver off-gas (DOG), solvent extraction vessel off-gas (VOG), and waste solidification off-gas. An analysis of the distribution of iodine between aqueous separations unit operations found that 95–99% of total iodine release to the off-gas occurs during dissolution, releasing iodine into the DOG, and also found that much of the balance of the iodine is released during solvent extraction, releasing the iodine into the VOG (Jubin et al. 2013). To achieve DFs greater than 1,000, the treatment of the plant off-gas streams must include, at minimum, the treatment of both DOG and VOG.

Removing iodine from the DOG has been the subject of substantial research and development in recent years. Iodine is primarily present in the DOG as elemental iodine (I_2) and is typically removed by using silver-based sorbent materials or aqueous caustic scrubbing. Interest in removing iodine from the VOG has also recently increased, and a 2015 analysis showed that the iodine speciation in the VOG primarily comprises organic alkyl iodides and that abatement technology for organic iodides is not well developed (Bruffey et al. 2015). Furthermore, the concentration of iodine in the VOG (parts per billion by volume levels) is substantially lower than that of the DOG (parts per million by volume levels), and the characteristics of the two gas streams differ in total flow rate, volume, and composition.

Because iodine abatement within the VOG might be a critical requirement for an eventual reprocessing facility, the relative lack of knowledge that surrounds iodine removal from the VOG prompted the US Department of Energy's Office of Nuclear Energy to initiate experimental efforts targeted at understanding organic iodide removal from prototypic VOG streams. At Oak Ridge National Laboratory (ORNL), this effort has focused on developing a comprehensive understanding of iodine removal from VOG streams by using silver-based sorbents (Jubin et al. 2017, Jubin et al. 2018, Bruffey et al. 2018). Variables such as the mass transfer zone of the sorbent bed, gas velocity, sorbate concentration, and sorbate speciation are being explored to determine their effects on iodine removal from VOG streams. One important aspect of this testing is developing an understanding of how the sorption of methyl iodide (CH_3I), the most studied organic iodide species to date, compares with the sorption of other volatile organic iodide species potentially present in the VOG. Tests at ORNL and Idaho National Laboratory (INL) have investigated the sorption of the longer chain alkyl iodides iodobutane (C_4H_9I) and iodododecane ($C_{12}H_{25}I$) to understand how iodine speciation might affect iodine sorption by silver-based sorbents (Bruffey et al. 2019).

The experiments described in this report were conducted as part of the larger effort to understand organic iodine removal from the VOG. This work aimed to incorporate effluent monitoring into ORNL testing to

[a] $\mathrm{DF} = \frac{concentration\ of\ radionuclide\ in\ a\ control\ device\ inlet\ gas}{concentration\ of\ radionuclide\ in\ a\ control\ device\ outlet\ gas}$

provide more insight into the reaction pathways of C_4H_9I sorption by silver mordenite (AgZ), a common silver-based zeolite mineral sorbent. Much of the testing at ORNL to date has been limited to continuous weight measurements via a custom thermogravimetric analyzer (TGA) and posttest sorbent analysis for total iodine content. These measurements provide insight into loading rates and sorbent iodine capacity values across a range of operating conditions, but they cannot provide insight into the specific sorption mechanisms that drive sorption rates or capacities.

The experiments described in this report extend the current understanding of organic iodide sorption by zeolites. The literature reflects knowledge of the reaction pathways that govern CH_3I sorption, but it does not address whether similar pathways can be validated for other iodine-bearing species. This work reflects initial testing that will continue to be developed, and an end-of-year report will detail the final results of the multiyear testing campaign designed to understand iodine mitigation from VOG streams.

2. BACKGROUND

There is a dense body of literature surrounding the sorption of organic iodides, primarily CH_3I, by silver-based sorbents, as documented in a review article by Huve et al. (2018). A formal review of this information is outside the scope of this report, but relevant portions are discussed in this section to provide an understanding of the test aims and experimental approach.

Some of the earliest documentation of potential sorption pathways for CH_3I by AgZ is found in Scheele et al. (1983). Scheele et al. tabulated the free energies of many relevant reactions, including those of I_2 sorption by AgZ with and without the presence of NO_x gas in the initial feed stream. Huve et al. (2018) provides a more condensed list of potentially applicable reactions. Reactions from these papers are provided in Table 1, and the free energies are updated in this document by using the thermodynamic calculation software HSC Chemistry Version 9 (Outotec 2018) for three temperatures. Studies also show that the sorption of CH_3I by AgZ is catalyzed by the zeolite surface itself (Nenoff et al. 2014). This is reflected in Table 1 by the inclusion of Reaction 0, a decomposition of CH_3I to a CH_3–zeolite complex. The CH_3–zeolite complex can then continue to react to form methanol (CH_3OH) or other organic compounds. Catalysis of CH_3I by the zeolite surface might facilitate some or all of equations 1–6 in Table 1.

Table 1: Proposed CH_3I sorption pathways. *Synthesized from Scheele et al. (1983) and Huve et al.(2018)*.

Equation	Proposed sorption reactions	$\Delta G_{reaction}$ *(kcal)*		
		300 K	400 K	500 K
0	CH_3I + Ag-zeolite ↔ CH_3-zeolite + AgI	Not tabulated		
1	$2Ag + 2CH_3I(g) \rightarrow 2AgI + C_2H_6(g)$	-46.9	-43.9	-41.5
2	$Ag^0 + CH_3I(g) + H_2O(g) \rightarrow AgI + CH_3OH(g) + 1/2H_2$	-7.6	-4.6	-2.4
3	$Ag + CH_3I(g) + CH_3OH \rightarrow AgI + CH_3OCH_3(g) + 1/2H_2$	-15.7	-11.7	-8.5
4	$Ag^+(aq) + CH_3I(g) + H_2O(g) \rightarrow AgI + CH_3OH(g) + H^+(aq)$	-22.2	-18.3	-14.7
5	$7NO + 2CH_3I(g) \rightarrow I_2(g) + 2CO_2 + 3H_2O(g) + 7/2N_2$	-500.4	-499.1	-497.8
6	$7NO_2(g) + 4CH_3I(g) \rightarrow I_2(g) + 4CO_2 + 6H_2O(g) + 7/2N_2$	-398.4	-404.4	-410.5

In Reactions 1–4, the iodine-bearing absorbed species is solid silver iodide (AgI), which can be present in multiple crystalline forms, depending on specific sorption conditions (Chapman et al. 2010). Beyond AgI production, several key organic byproducts could also be present, depending on the reaction pathway. Reaction 1 produces ethane (C_2H_6), Reaction 2 produces CH_3OH, and Reaction 3 provides a pathway for the CH_3OH to further react and form dimethyl ether (DME).

In Reactions 5 and 6, AgI is not identified as the product, and the NO (Reaction 5) or NO_2 (Reaction 6) reactant serves to facilitate the production of free I_2. This I_2 could be assumed to continue to react and adsorb onto the AgZ, indicating that more complex reaction pathways will be present in NO_x-bearing gas streams.

These proposed reactions have been supported through the observation of the suggested byproducts in the gaseous effluent streams of CH_3I sorption experiments. INL has verified the presence of CH_3OH and DME in the effluent streams of CH_3I/AgZ sorption experiments (Soelberg and Watson 2016), validating Reactions 2 and 3. Chebbi et al. (2016) also reported CH_3OH and DME in the effluents of similar sorption testing.

Additional studies have been added to the literature surrounding the fundamental mechanisms and characteristics of CH_3I sorption by AgZ or other zeolites (Azambre et al. 2017, Chebbi et al. 2017, Huve et al. 2018, Tang et al. 2020, Chebbi et al. 2021). One remaining question relates to the role of water in the CH_3I/AgZ sorption reaction. Chebbi et al. (2021) describes some of the published conflicting studies on the role of water in the sorption of CH_3I by AgZ. Recent studies by ORNL confirm that water plays less of a role in CH_3I sorption than initially thought, despite a significant difference in observed loading rates, depending on whether water is present in the gas feed stream. Greaney et al. (2020) found no statistical difference observed in the loading capacity of AgZ for CH_3I from dry and humid gas streams. The findings of Greaney et al. (2020) broadly align with the findings of Chebbi et al. (2021).

The work described here focuses on the sorption of C_4H_9I by AgZ and attempts to determine whether the sorption reactions that govern CH_3I can be translated to the sorption of C_4H_9I. Specifically, the authors hypothesized that the sorption of C_4H_9I by AgZ will result in the formation of butanol (C_4H_9OH). A series of thin and deep bed sorption tests were performed, and the gaseous effluents were analyzed by gas chromatography (GC) coupled to a mass spectrometer (MS). Given the uncertainties surrounding the impact of water on organic iodine sorption, experiments were performed by using dry and humidified feed gas streams. Future reports will use these data to provide insights into organic iodide removal from VOG streams across a spectrum of fundamental and applied scales.

3. METHODS

Experimental methods included exposing thin and deep beds of reduced AgZ to dry and humid iodine-bearing feed streams. Effluent monitoring of the sorbate (C_4H_9I) and potential organic product (C_4H_9OH) was performed by gas chromatography-mass spectrometry (GC-MS). Validating experimental methodology included some testing with CH_3I as the sorbate, and in these tests, CH_3I and CH_3OH were monitored. Although DME is also known to be produced in the sorption of CH_3I by AgZ, its release is near simultaneous with CH_3OH, and it is of lower abundance (Chebbi et al. 2021). Thus, monitoring for CH_3OH or C_4H_9OH was judged sufficient to confirm reaction pathways.

3.1 Experimental Methods

AgZ 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. Before use in testing, the sorbent material was dried at 270°C under flowing argon gas for 3 days. It was then reduced by 10 day exposure to a flowing H_2–N_2 (4–96%) blend gas at 270°C.

A test system was designed so that two beds could be loaded simultaneously and their effluents could be sampled for GC-MS analysis (Figure 1). Columns with 2.73 in. internal diameter were used, and the flow rate was kept constant at 3.94 LPM. One column received humid air or dry air, and the second column received dry air. All sorbent loading was conducted at 150°C, and the burn-off temperatures of two tests reached 225°C. Nitrogen-sparged bubblers were used to generate the organic species of interest (i.e., CH_3I, C_4H_9I, or C_4H_9OH). The inlet concentrations of the monitored products were verified through GC-MS analysis.

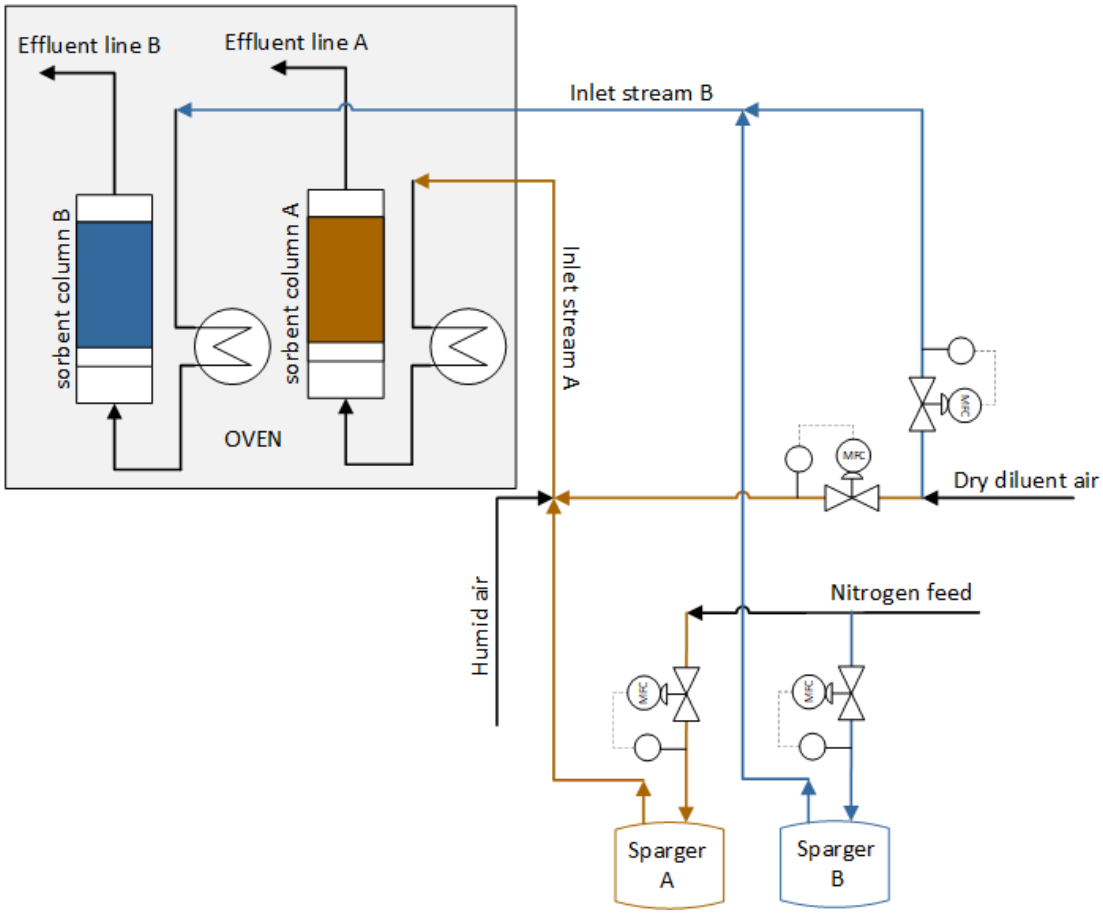

Figure 1. Diagram of experimental setup.

Multiple downstream sampling systems were tested for GC-MS analysis, including solid phase microextraction (SPME) fibers, capturing the effluent in flow-through gas-tight sampling vials and directly sampling the effluent with a gas-tight syringe. The SPME fibers were difficult to clean, which resulted in carryover between samples. The flow-through sampling vial resulted in imprecise data when it was used with one concentration gas stream. The most accurate and precise sampling method was determined to be the direct sampling of the effluent by using headspace syringes.

3.2 Analytical Methods

Effluent samples were analyzed on an Agilent 8890-5977B GC-MS with a 30 m DB-624-UI ultra-inert capillary column. The GC method was designed to capture iodoalkanes ranging from methyl to dodecyl iodide. The inlet temperature remains at 250°C while the column temperature starts at 30°C for 5 minutes before ramping to 220°C at a rate of 10°C/minute before holding at 220°C for 6 minutes. Helium is used as the carrier gas with a constant flow rate of 1.2 ml/min. The column effluent is analyzed on a single-quad mass spectrometer and the data are analyzed using the Agilent MassHunter software. Manual injections were of 200 µl sample volumes were done with gas-tight syringes. Methanol is detected on the chromatograph at 3 min, CH_3I is detected at 4.5 min, C_4H_9OH is detected at 10.1 min, and C_4H_9I is detected at 13.2 min (Figure 2). An additional ramp temperature of 30 min to 220°C is included to ensure that C_4H_9OH fully burns off the column and is not carried over from sample to sample. Column and syringe backgrounds were analyzed at least once daily (often multiple times a day) by injecting 200 µl of room air into the GC-MS and running the aforementioned method.

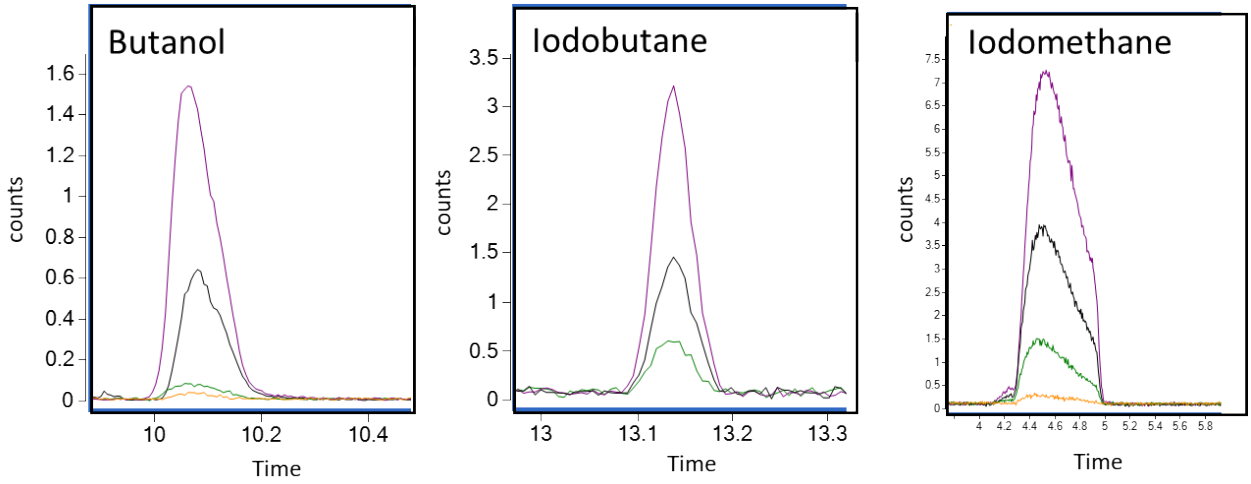

Figure 2. Chromatographs showing examples of calibration standards analyzed. The *y*-axis is the counts (not to scale between figures), and the *x*-axis is time. Purple is 100 ppm, black is 50 ppm, green is 10 ppm, and orange is 1 ppm.

Gas-phase calibration standards were created by using the same sampling methods as the experiments. Standards were created at 1, 10, 50, and 100 ppm. Peak areas integrated by the Agilent MassHunter software are used for quantification. Limits of detection (LODs) and limits of quantification (LOQs) were determined for each species using chromatograph baseline statistics and regression statistics from the calibration curve generated by the standards (Table 2). For reference, the vapor pressures of each compound are also included in Table 2. A 1 ppm standard was not analyzed for iodobutane. Iodomethane does not form a gaussian peak in the chromatograph, possibly due to effects of the compound interacting with the column. This peak broadening is routinely observed for iodomethane across experiments.

Table 2: LODs and LOQs for monitored species.

Species	LOD (ppm)	LOQ (ppm)	Vapor pressure (mmHg)
CH_3I	0.06	0.13 ± 0.06	400 (20°C)
CH_3OH	Not determined	Not determined	90 (25°C)
C_4H_9I	1	12 ± 1	0.138 (25°C)
C_4H_9OH	3	4 ± 1	4.35 (20°C)

3.3 Completed Tests

Seven tests are reported here, and a summary of test conditions is shown in Table 3; more detailed information is provided in Section 4.

Table 3. Matrix of test conditions.

SM test #	Species	Inlet conc. (ppm)	Sorbent	Temp. (°C)	Dew point (°C)	Carrier gas	Bed height (in.)	Bed Mass (g)
FY21-SM-2	C_4H_9I	20	Ag^0Z	150	-70	Air	2	45
FY21-SM-3	C_4H_9I	20	Ag^0Z	150	10	Air	2	45
FY21-SM-4	C_4H_9I	50	Ag^0Z	150	-70	Air	1	18
FY21-SM-5	C_4H_9I	50	Ag^0Z	150	0	Air	1	18
FY21-SM-6	C_4H_9I	50	Ag^0Z	150	0	Air	0.25	4
FY21-SM-7	C_4H_9OH	50	Ag^0Z	150	-70	Air	0.25	4
FY21-SM-8	CH_3I	50	Ag^0Z	150	10	Air	0.3	6

4. OBSERVATIONS

4.1 SM-2 and SM-3: C_4H_9I Deep Bed Tests

Initial tests to evaluate whether C_4H_9OH formed during sorption were conducted in deep sorbent beds (~45 g of AgZ in 2 in. deep bed). One dry test (SM-2) was conducted at 150°C, -70°C dew point, and 20 ppm C_4H_9I in air, and one humid test (SM-3) was conducted at 150°C, 10°C dew point, and 20 ppm C_4H_9I in air. The dry test ran for 12 days, and the humid test ran for 10 days, allowing portions of the sorbent beds to approach iodine loadings near capacity. The effluent was sampled for GC-MS analysis multiple times on the first day and then daily thereafter. Neither test resulted in detectable C_4H_9I breakthrough of the 2 in. deep bed.

The results of these tests were inconclusive. A transient C_4H_9OH peak and a cyclobutanol peak were detected in chromatographs from the wet and dry tests. A C_4H_9OH peak was present at the 46 h sample and 96 h sample but was absent from the 69 h sample. However, further analysis of the GC column and syringe background found that the observed C_4H_9OH might have been a contamination product from unrelated experimental samples that were being analyzed with GC-MS. Column backgrounds were determined by running the GC-MS method with no injection. Syringe backgrounds were determined by sampling 200 µL of room air and analyzing that injection with the set GC-MS method (Figure 3). Ultimately, the validity of the C_4H_9OH results could not be determined for these tests. Additional testing was not performed until other projects that cause potential interferences were completed.

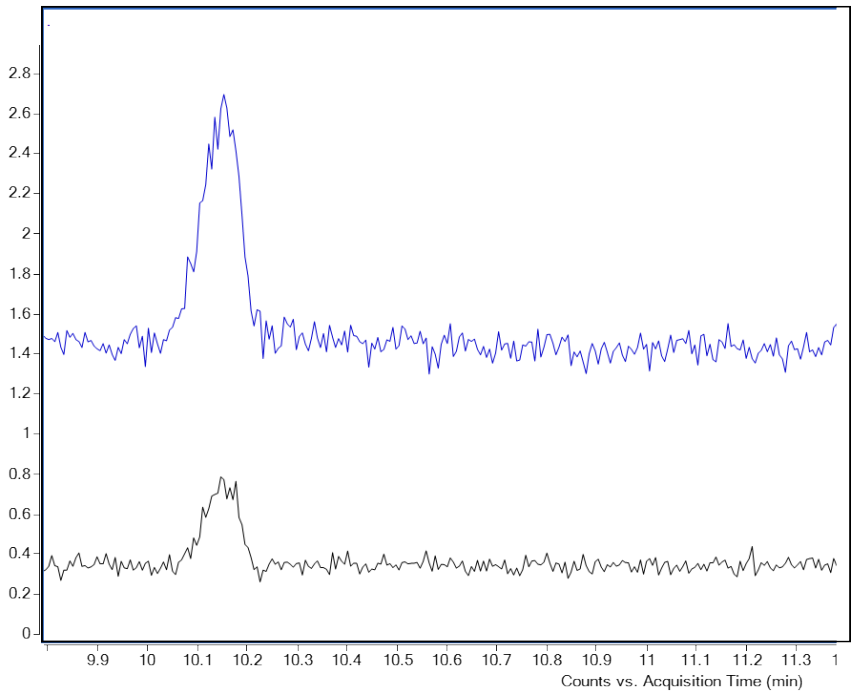

Figure 3. Chromatograph showing a syringe background sample (black, ~6 ppm) and an effluent sample from the humid SM-3 test (blue, ~12 ppm). C_4H_9OH (peak at 10 min) is present in both samples, suggesting that contamination from the syringe could account for C_4H_9OH signals observed in the effluents of SM-2 and SM-3.

4.2 SM-4 and SM-5: C_4H_9I Thin Bed Tests

The goal of these tests was to determine whether C_4H_9OH was present in the test effluent. The tests were designed to run until a C_4H_9I breakthrough was observed. One thin bed test was run with a dry air stream at a dew point of -65°C, and the second thin bed test was run under a humid air stream at a dew point of 0°C. Both tests used 18 g of AgZ (~1 in. deep) and a 50 ppm C_4H_9I inlet stream. The dry test (SM-4) ran for 30 h, and the humid test (SM-5) ran for 72 h. In the dry test, the inlet concentration was increased to 100 ppm after 24 h in an attempt to increase the concentration of any potential reaction products for easier detection. In the humid test, the concentration was held constant at 50 ppm for the 72 h test.

No C_4H_9OH or other reaction products were detected in the dry test under a 50 ppm stream or a 100 ppm stream. After 29 h, C_4H_9I breakthrough was observed.

Similarly, in the humid test, no C_4H_9OH was detected in any of the 10 effluent samples analyzed over 3 days. C_4H_9I breakthrough was detected in the effluent at 72 h.

4.3 SM-6 and SM-7: C_4H_9I and C_4H_9OH Burn-Off Tests

With no detection of C_4H_9OH in the effluents of SM-4 and SM-5, consideration was given to the potential that C_4H_9OH might be produced and subsequently be retained by the sorbent bed. The goal of tests SM-6 and SM-7 was to determine whether C_4H_9OH initially adsorbed to the AgZ during loading and could be removed at an elevated temperature. To test this possibility, C_4H_9OH was passed through a bed of AgZ at 150°C to establish any sorption. The C_4H_9OH flow was then discontinued, and the bed temperature was

increased to 225°C while effluent samples were collected. An C_4H_9I loaded test was sampled at the same temperature profile for comparison.

In test SM-6, a thin bed of AgZ (4 g total mass) was contacted with a humidified gas stream that contained 50 ppm C_4H_9I for 168 h (Table 3). Effluent samples were collected downstream of the thin bed repeatedly to measure the breakthrough concentration. Throughout the loading period, the mean downstream effluent C_4H_9I concentration was 41 ppm.

In test SM-7, a thin bed of AgZ (4 g total mass) was contacted with a dry gas stream that contained 50 ppm C_4H_9OH for 48 h (Table 3). Effluent samples were collected downstream of the thin bed during loading to measure the breakthrough concentration. Concentrations of 25 ppm were detected in the downstream effluent after 2 h, 43 ppm were detected downstream after 30 h, and 31 ppm were detected downstream after 48 h. This fluctuating concentration is not readily explained. The downstream concentrations are lower than the inlet concentration, suggesting that C_4H_9OH was being adsorbed to the AgZ during the loading phase.

After loading, the beds were purged with dry air at 150°C. Over the course of several hours, the bed temperature was increased to 160, 175, 200, and 225°C with effluent samples collected at each temperature (Table 4). The boiling point of C_4H_9OH is 117°C, which is well below the final temperature of the sorbent bed. Literature indicates that C_4H_9OH adsorbed on other similar zeolites will release at temperatures well below 200°C (Oudshoorn et al. 2012).

Table 4. Results of C_4H_9I and C_4H_9OH burn-off tests.

GC sample	Effluent sample	Temp. (°C)	C_4H_9OH (ppm)	C_4H_9I (ppm)
1	SM-6 C_4H_9I (loading)	150	BDL	46
2	SM-7 C_4H_9OH (loading)	150	31	--
Stop C_4H_9I flow, continue air diluent				
3	SM-6 C_4H_9I	150	BDL	21
Stop C_4H_9OH flow, continue air diluent				
4	SM-7 C_4H_9OH	150	3	--
Raise temperature to 160°C				
5	SM-6 C_4H_9I	160	BDL	16
6	SM-7 C_4H_9OH	160	BDL	--
Raise temperature to 175°C				
7	SM-6 C_4H_9I	175	BDL	14
8	SM-7 C_4H_9OH	175	BDL	--
Raise temperature to 200°C				
9	SM-6 C_4H_9I	200	BDL	BDL
10	SM-7 C_4H_9OH	200	BDL	--
Raise temperature to 225°C				
11	SM-6 C_4H_9I	225	BDL	BDL
12	SM-7 C_4H_9OH	225	BDL	--

4.4 SM-8: CH_3I Loading and Burn-Off

One experiment was completed to determine whether CH_3OH was detected during CH_3I sorption on a thin bed of AgZ under humid conditions (Table 3). Fifty parts per million of CH_3I in air was loaded on a thin bed of AgZ at 150°C and a dew point of 10°C. Loading was initiated at a dew point of 0°C but was raised to 10°C after several hours. After 2 days of loading, the CH_3I flow was stopped, and air was purged through the bed as the temperature was raised in 25°C increments to 225°C. The effluent was sampled at each temperature increment.

During the loading portion of the test at 150°C, transient CH_3OH was identified in effluent in the 10°C stream but not in the 0°C stream. The observed CH_3OH was detected at the correct mass to charge ratio and retention time, but did not form a statistically significant peak (2σ above baseline) and could not be quantified.

During the loading portion of the test at 150°C, 50 ppm of CH_3I was consistently detected downstream of the bed. That is, only a fraction of CH_3I present in the feed stream was sorbing to the AgZ during the loading period. This would be expected in a thin bed test in which the concentration of sorbate is assumed to be nearly unchanged across the bed. In contrast, the SM-6 C_4H_9I thin bed test, which ran under similar conditions (150°C, 0°C dew point, identical flow rates, 4 g AgZ bed), recorded lower breakthrough concentrations with a mean of 41 ppm. This suggests that C_4H_9I sorbs onto AgZ differently than CH_3I. These data support observations from TGA testing that show AgZ experiencing a faster initial weight gain and reaching saturation more quickly for C_4H_9I sorption than for CH_3I sorption (Figure 4).

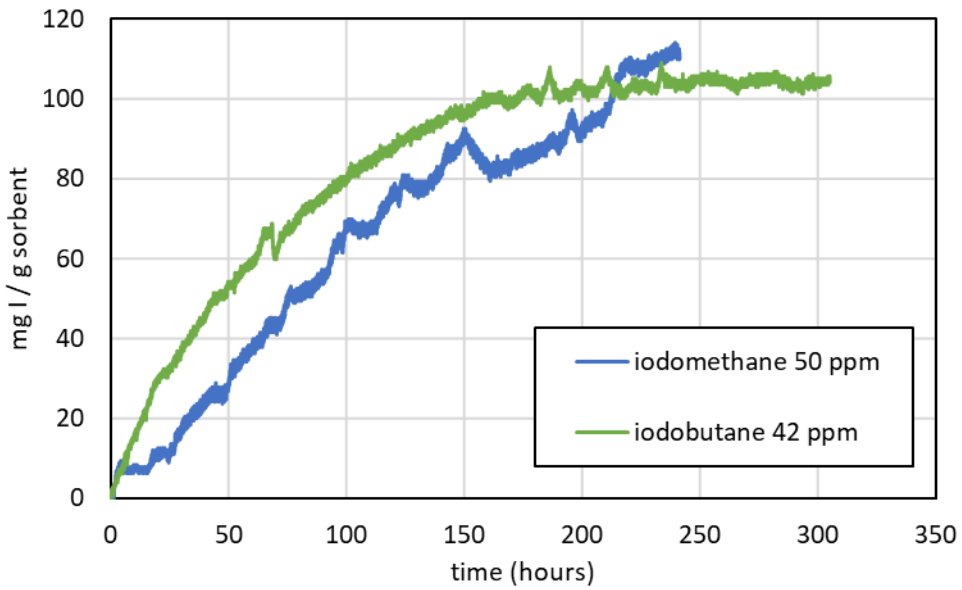

Figure 4. Loading rates of CH_3I and C_4H_9I on thin bed tests recorded by TGA.

During the burn-off portion of the test, no CH_3I or CH_3OH was detected in the effluent stream. As soon as the CH_3I loading flow was stopped, it disappeared from the effluent. This contrasts with the similar C_4H_9I test (SM-6) in which C_4H_9I was detected in the effluent stream for a few hours after the flow was stopped (between 150°C and 175°C) (Table 4). This observation could indicate higher levels of physisorption for C_4H_9I on AgZ compared with CH_3I.

5. CONCLUSIONS AND FUTURE TESTS

Thin bed CH_3I tests conducted at a 10°C dew point resulted in the identification of CH_3OH in the chromatograph at levels near the LOD, confirming literature observations and the experimental methodology used in these studies. To bolster this observation, testing with greater masses of sorbent can be performed to increase the amount of sorbent available for reaction and the corresponding amount of CH_3OH produced to well above the LOQ.

C_4H_9I and CH_3I show different loading rates in TGA tests and thin bed tests in which the effluent is analyzed downstream of the test. C_4H_9I sorbs to AgZ more quickly than CH_3I. C_4H_9I is also released from the sorbent during burn-off, whereas CH_3I is not.

Thin bed C_4H_9I tests conducted at -65°C and a 0°C dew point did not result in C_4H_9OH detection in the effluent, strongly indicating that C_4H_9I sorption follows a different reaction pathway than CH_3I sorption.

To finalize this experimental thrust before completing the comprehensive VOG testing program, select additional data will be collected. These actions will include: (1) determining the iodine content of each AgZ bed used in testing and (2) replicating SM-7 and SM-8 by using deep beds of AgZ to ensure that any CH_3OH and C_4H_9OH produced are above the LOQ. These results will be included in the final end-of-year report.

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