Joint Test Plan for the Evaluation of Iodine Retention for Long-Chain Organic Iodides

Nuclear Technology Research and Development

Approved for public release. Distribution is unlimited

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign

R. T. Jubin, S. H Bruffey (ORNL)
N. R. Soelberg, A. K. Welty (INL)

Oak Ridge National Laboratory
28 February 2018
NTRD-MRWFD-2018-000212
ORNL/SPR-2018/781

DISCLAIMER

This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness, of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trade mark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

SUMMARY

A number of reports have identified four volatile radionuclides that arise from the reprocessing of nuclear fuel (^{3}H, ^{14}C, ^{85}Kr, and ^{129}I) that require controls limiting their environmental release from reprocessing facilities in order to meet US regulatory requirements. Of these, ^{129}I has the longest half-life and highest potential biological impact.

The study of inorganic iodide in aqueous reprocessing facility off-gas systems has been almost exclusively limited to I_2, and the focus of organic iodide studies has been CH_3I as a surrogate for various organic iodides that could be present. A study conducted in 2015 focused on those inorganic and organic iodine-bearing species in reprocessing plants that have the potential to be poorly sequestered with traditional capture methods. This study found that even if high decontamination factors (DFs) are achieved for the dissolver off-gas (DOG), losses of iodine to the head-end cell, if greater than about 0.1% of the total iodine inventory, can limit the overall plant DF unless sufficiently high DFs are also achieved for the cell off-gas. The same is true for the losses of iodine to the vessel off-gas (VOG), if those losses are greater than about 0.1%. The study further indicated that high DFs on the VOG may be difficult to achieve as it is the stream where penetrating, or difficult to remove, organic iodide species are most likely. These two factors prompted studies examining organic iodide removal from prototypic VOG streams at both Oak Ridge National Laboratory (ORNL) and Idaho National Laboratory (INL). These studies included an initial evaluation of reduced silver-exchanged mordenite (Ag^0Z) and silver-functionalized silica-aerogel (AgAerogel) for the capture of CH_3I and I_2 under VOG conditions by Jubin et al. (2017a) and for the capture of iodobutane under DOG conditions at INL (to be reported in 2018.)

The objective of this report is to develop a robust experimental program that will evaluate the adsorption rate of long-chain organic iodides and identify any significant variations in mass transfer zone and by-products produced during the adsorption on Ag^0Z and AgAerogel under both DOG and VOG conditions expected for a used nuclear fuel aqueous reprocessing facility. Organic species of interest include both short-chain alkyl iodides such as methyl iodide (CH_3I) and longer alkyl iodides up to iodododecane ($C_{10}H_{21}I$). The primary product of this report is a test plan for the experimental work that could be conducted as part of the ongoing off-gas abatement R&D efforts at both INL and at ORNL.

This page is intentionally left blank.

CONTENTS

FIGURES

TABLES

This page is intentionally left blank.

ACRONYMS

AgAerogel	silver-functionalized silica-aerogel
AgZ	silver-exchanged mordenite
Ag^0Z	hydrogen-reduced silver-exchanged mordenite
DF	decontamination factor
DOG	dissolver off-gas
EDS	energy-dispersive spectroscopy
GC	gas chromatography
GC-MS	gas chromatography–mass spectrometry
GC-FID	gas chromatography with flame-ionization detection
INL	Idaho National Laboratory
MFC	mass flow controller
MTZ	mass transfer zone
NAA	neutron activation analysis
ORNL	Oak Ridge National Laboratory
SPME	solid-phase microextraction
TBP	tri-*n*-butyl phosphate
TGA	thermogravimetric analysis
UNF	used nuclear fuel
VOG	vessel off-gas

This page is intentionally left blank.

JOINT TEST PLAN FOR THE EVALUATION OF IODINE RETENTION FROM LONG-CHAIN ORGANIC IODIDES

1. OBJECTIVE

The objective of this report is to develop a robust experimental program that will evaluate the adsorption rate of long-chain organic iodides by reduced silver-exchanged mordenite (Ag^0Z) and silver-functionalized silica-aerogel (AgAerogel) and identify any significant variations in mass transfer zone (MTZ) and by-products produced during the adsorption under both dissolver off-gas (DOG) and vessel off-gas (VOG) conditions expected for a used nuclear fuel (UNF) aqueous reprocessing facility. The primary product of this report is a test plan for the experimental work that could be conducted as part of the ongoing off-gas efforts at both the Idaho National Laboratory (INL) and the Oak Ridge National Laboratory (ORNL).

2. BACKGROUND

A number of reports have identified four volatile radionuclides that arise from the reprocessing of nuclear fuel (^3H, ^{14}C, ^{85}Kr, and ^{129}I) that require controls limiting their environmental release from reprocessing facilities in order to meet US regulatory requirements (Jubin et al. 2011a, 2012, Bruffey et al. 2015). Of these, ^{129}I has the longest half-life and highest potential biological impact. Current US Environmental Protection Agency regulations governing nuclear facilities (40 CFR 190) state that the total quantity of radioactive materials entering the general environment from the entire uranium fuel cycle, per gigawatt-year of electrical energy produced by the fuel cycle, must contain less than 5 mCi of ^{129}I. Previous studies have shown that the overall plant decontamination factor (DF) for ^{129}I during aqueous used fuel reprocessing must, at minimum, exceed 1,000 to meet regulatory requirements.

The study of inorganic iodide in aqueous reprocessing facility off-gas systems has been almost exclusively limited to I_2, and organic iodide studies have been focused on methyl iodide (CH_3I) as a surrogate for various organic iodides that could be present. A study by Bruffey et al. (2015) focused on those inorganic and organic iodine–bearing species in reprocessing plants that have the potential to be poorly sequestered with traditional capture methodologies. These forms have historically been called *penetrating* iodine-bearing species. Based on the results of the literature survey and some limited thermodynamic modeling, the inorganic iodine species hypoiodous acid (HOI) and iodine monochloride (ICl) were identified as potentially low-sorbing iodine species that could be present in off-gas systems. Primarily inorganic iodine compounds were also expected from waste management processes, including chlorinated species such as ICl.

Organic species of interest included both short-chain alkyl iodides such as CH_3I and longer alkyl iodides up to iodododecane ($C_{10}H_{21}I$). It was found that fuel dissolution may provide conditions conducive to HOI formation and has been shown to result in volatile short-chain and long-chain alkyl iodides, although these may not volatilize until later in the reprocessing sequence. Solvent extraction processes were found to be significant sources of various organic iodine-bearing species. Discussions between the authors of this test plan and several solvent extraction experts at DOE national laboratories during 2017 confirmed that likely organic iodides could include alkyl iodides up to iodobutane (from iodizing radiolytic degradation products of the organic solvent tri-*n*-butyl phosphate [TBP]) and alkyl iodides up to iodododecane (from iodizing radiolytic degradation products of the dodecane or kerosene carrier/diluent). This information initiated an evaluation of the capture of iodobutane by AgZ under DOG conditions at INL (to be reported in 2018.)

To understand the importance of capturing penetrating forms of iodine, a calculation of the overall plant DF was carried out by estimating the iodine splits, speciation, and individual DFs for each off-gas stream within the aqueous reprocessing plant. This analysis led to several key observations. First, even if high DFs are achieved for the DOG, losses of iodine to the head-end cell, if greater than about 0.1% of the total iodine inventory, can limit the overall plant DF unless sufficiently high DFs are also achieved for the cell off-gas. The same is true for the losses of iodine to the VOG, if those losses are greater than about 0.1%. Second, the

VOG DF may be limiting to the overall plant DF as it is the stream where penetrating, or difficult to remove, iodine species are most likely. Third, the contributions from penetrating forms of iodine to the plant DF are largely unknown; the overall plant DF would depend strongly on the possible DF value that can be achieved for these penetrating forms at each off-gas stream, if those penetrating forms total more than about 0.1% of the total iodine inventory.

Iodine-containing off-gas will be present in the DOG, the cell off-gas, the VOG, the waste off-gas, and the shear off-gas (Jubin et al. 2013). The VOG will most likely contain 1–5% of the total iodine at concentrations of parts per billion by volume (ppbv). A number of studies have examined iodine abatement from the DOG, which contains greater than 95% of the iodine inventory of the plant, but very few have examined the recovery of iodine from the VOG stream.

Silver-exchanged mordenite (Ag^0Z) has been considered a promising iodine sorbent for use in UNF reprocessing plants, and AgAerogel is being studied as a potential alternative. Haefner et al. (2009) conducted initial iodine adsorption tests with I_2 concentrations nominally 25 ppb and 1 ppm using unreduced commercial silver mordenite. DFs exceeding 100 were reported for the 25 ppb tests, and DFs exceeding 10,000 were reported for the 1 ppm tests. For selected tests, moisture content was varied up to about 1.5 vol% (13˚C dew point), adsorption temperature was varied from 25–150˚C, and NO_x concentration was varied from 0–1,000 ppm.

Jubin et al. (2017a) conducted an initial evaluation of the performance of Ag^0Z and AgAerogel under VOG conditions. Both I_2 and CH_3I adsorption tests were conducted with Ag^0Z and AgAerogel at a range of concentrations up to 1,000 ppb. These experiments were performed with two specific aims: (1) to assess the effect of iodine concentration on its adsorption by the sorbent and (2) to compare the performance of Ag^0Z and AgAerogel in the removal of iodine from a prototypical VOG stream. Results shown by Jubin et al. (2017a) indicate that the concentration of CH_3I within the range studied (40–1,000 ppb CH_3I) does not appear to affect either the maximum observed iodine loading for the sorbent or the penetration of CH_3I into the Ag^0Z sorbent bed. Similar testing performed on the adsorption of CH_3I by AgAerogel showed the same lack of dependence on CH_3I feed concentration.

At the low iodine concentration expected in the VOG stream (<50 ppb), testing using prototypical off-gas concentrations results in test durations of 1–4 months to achieve iodine loading of the sorbent bed at levels detectable by neutron activation analysis (NAA). Based on the tests reported, the lack of dependence on feed concentration observed in Jubin (2017a) could provide a technical basis for accelerated testing (by using somewhat higher concentrations of iodine species than the expected VOG concentration range). These accelerated tests using higher organic iodide concentrations may allow a reduction in the need to perform numerous extended duration tests using very low iodine feed concentrations (7–40 ppb). However, previous studies have also shown that the sorbent will age, or experience a decrease in total iodine capacity, while online for the durations expected for the VOG bed life of 4+ months (Jubin 2011b). As a result, any accelerated test must be qualified to note that in situ aging effects may reduce the observed loadings.

Jubin et al. (2017a) also compared the penetration depth of CH_3I into a sorbent bed for both AgZ and AgAerogel as a function of CH_3I concentration. Those tests indicated that CH_3I at these sub-ppm concentrations does not necessarily penetrate the sorbent bed to a depth greater than that of I_2. However, a visual examination of the iodine loading profiles reveals a greater fraction of recovered iodine present in the tails of the penetration curves for CH_3I tests versus I_2. The percent of iodine retained in the first 2 cm of sorbent in the test system showed an inverse relationship to the penetration depth in the AgAerogel.

The second aim of these tests was to compare the performance of Ag^0Z and AgAerogel in VOG conditions. Ag^0Z and AgAerogel iodine adsorption performance was examined for two I_2 concentrations (7 and 500 ppb) and three CH_3I concentrations (40, 400, and 1,000 ppb). The most notable difference between the two sorbents is that in all cases for both iodine species the maximum observed iodine loadings were higher for AgAerogel. This was observed in thin-bed testing performed at higher concentrations. However, if the iodine loading data are normalized to account for the higher silver content in the AgAerogel, then no clearly discernable differences existed between the two sorbents.

Although the preliminary loading data were similar, the mechanical performance for the two sorbents was notably different. Little or no mechanical degradation was observed for the Ag^0Z. However, during the course of each test a notable amount of fines were created from the AgAerogel material. Density measurements showed that the post-test bulk density of the AgAerogel was ~15% greater than that of the initial material. It was suggested that, along with increased mass and density from the adsorption of iodine, this increase in bulk density could be attributed to the breakdown of the larger aerogel structure into finer particles, resulting in bed compaction.

Throughout these tests, and particularly in the case of CH_3I adsorption tests, there was a significant discrepancy in the iodine material balances. This discrepancy does not appear to result from leaks or from concentration effects on the adsorption process. It was recommended that future work in this area should be focused on resolving the outstanding questions about the closure of the material balance. The first recommended step was to determine the extent of physisorption of CH_3I and the extent to which it is easily removed. This evaluation was initiated at ORNL in early FY 2018.

The second recommended objective should be determination of the length of the MTZ and saturation loadings under VOG conditions. These topics have not yet been investigated, as the low iodine concentrations present in the VOG stream prevent saturation from being measured using test durations of less than 1 year. This avenue of research now appears more promising based on the data on concentration effects and the potential to conduct accelerated testing. However, the results of accelerated tests may not account for any detrimental sorbent aging effects that could occur during longer duration testing.

3. TEST OBJECTIVES

A number of open questions regarding iodine adsorption by both Ag^0Z and AgAerogel from DOG and VOG streams containing long-chain organic iodides remain. For the VOG system, a report by Jubin et al. (2017b) identified the highest priority knowledge gaps regarding iodine adsorption to be the achievable DF and the length of the MTZ. Fundamental adsorption data such as the iodine saturation capacity on the sorbent and the rate of iodine adsorption were also gauged to be of high priority. Only limited data exist for the capture of any of these species on AgZ and Ag-Aerogel at DOG conditions. As noted above, a previous literature review by Bruffey, et al. (2015) indicated that dilute organic iodides present in the VOG stream would be more difficult to remove (i.e., more penetrating, than I_2). However, the data supporting this were relatively sparse. The initial testing by Jubin et al. (2017a) showed minimal differences between elemental or organic iodine adsorption from dilute streams by silver-based sorbents, but the material balance closure for the capture of CH_3I was more problematic than for elemental iodine.

Building upon an analysis of data gaps for off-gas systems completed in 2017 by Jubin et al. (2017b), this test plan will focus on the performance data needed for the iodine capture system. Of the 26 classes of data gaps identified in the 2017 study, the proposed test plan will focus on gaps 1–7.

3.1 Key Questions

This proposed effort is focused on a number of specific questions that span the range of organic iodide concentrations and species anticipated in the VOG and DOG. These principal questions are as follows.

1. Is the adsorption rate a function of hydrocarbon chain length?
2. Is the adsorption rate a function of long-chain organic iodide concentration?
3. What is the effect of the gas velocity on the behavior observed determined in questions 1–2?
4. What is the saturation concentration of iodine for various long-chain organic iodides on silver-based sorbents, and does it vary with target feed species?

5. What is the DF over a fixed length of bed as a function of concentration and iodine species in the feed gas?
6. If the adsorption rate changes, which is impacted the most: the DF, bed penetration depth, or bed penetration rate? (This is the combined effect of the results of questions 1, 2,3, and 5.)
7. What is the length and shape of the MTZ, and how do they vary or change for CH_3I and other organic iodides on silver-based sorbents?

As the data are collected to answer these primary questions, insight into several related questions can be obtained either by combining the results from several of the questions or by the collection and analysis of additional samples during the course of the experiments. These are as follows.

1. Does the amount of physisorption or ratio of physisorption to chemisorption vary with chain length and concentration?
2. What is the resulting form of the adsorbed iodine?
3. Is there an organic iodide concentration below which the sorbent becomes ineffective?
4. What is the effect of AgZ and AgAerogel on long-chain iodides, and can chemical speciation of organics and organic iodides exiting sorbent beds be determined?

3.2 Challenges

As pointed out by Jubin et al. (2017a), investigating these particular questions is inherently difficult given the nature of the VOG system. Providing and measuring extremely low concentrations of iodine present a challenge. Ensuring reliable delivery of iodine to the test system is complicated by the corrosive nature of iodine, which can foul gas regulators and generate deliquescent metal iodides in moist environments. Most importantly, very low iodine concentrations mean that it can take years to saturate even small amounts of sorbent. If the sorbent cannot be saturated, the MTZ of the bed cannot be determined. The VOG testing performed at ORNL to date has not saturated the silver sorbent with iodine (though a test designed to saturate part of a deep bed is under way and is expected to last at least 1 year). In an effort to provide an indication of the iodine distribution through the bed, previous studies have compared the depth of penetration of iodine into the sorbent bed.

Determination of another key engineering parameter, DF, is also very difficult in this system. First, to determine a DF of 1000 in a VOG system with 40 ppb CH_3I in the feed stream, iodine detection on the effluent would require quantification to parts-per-trillion levels. Analytical methodology for this type of effort requires a high degree of expertise. For example, the gas chromatography with flame-ionization detection (GC-FID), with solid-phase microextraction (SPME) injection, is used at INL to improve GC-FID detection limits by 0.1 to 0.01 compared to direct injection GC-FID. Still, the GC-FID with SPME injection can show a DF of about 1,000 only as long as the inlet organic iodide concentration is at least about 10 ppm. The detection limit for the GC-FID with SPME injection is about 10 ppb, and that value is rather noisy. Gas chromatography (GC) and gas chromatography–mass spectrometry (GC-MS) methods that use purge-and-trap injection techniques can achieve similar or better detection limits but are costly to use and require a high degree of expertise to achieve reproducible results.

Second, the analytical methodology should be able to analyze all possible iodine species present in the effluent gas. It is known that the decomposition of organic iodine species to I_2 or HI can be catalyzed by some sorbents, and if the sorbent has approached saturation and so cannot adsorb iodine from those species, then that iodine passes through the bed without being captured, even though the bed outlet organic iodide analysis incorrectly indicates high iodine capture (Nenoff et al., 2014). Thus, any measurement of iodine DF will be skewed if the analysis methods are incapable of measuring all iodine-bearing species present in the effluent.

Material balance closure will be difficult as a result of detection limit issues. To date, this has been based on a comparison of the calculated / assumed delivery amount (based on cylinder concentration certification or permeation tube release rate certification and gas flow measurements) with the NAA of subsamples of the iodine-loaded sorbent beds.

4. REQUIRED DATA AND TEST PLANS TO SYSTEMS AND PROPOSED APPROACHES

This section discusses the proposed experimental approach that could be used to address each question, the test conditions, and the data to be obtained. These questions need to be addressed for both AgZ and AgAerogel.

4.1 Data to Be Obtained

In general terms there are six classes of data to be obtained. These are as follows.

1. Adsorption rate data: This will be reported in terms of mg of I adsorbed / gm sorbent / unit time. This will also be reported in terms of per unit silver in the sorbent to provide a normalized result of active reactant. For the higher iodine/iodide feed concentrations (>500 ppb), these data will be obtained using existing thermogravimetric analysis (TGA) equipment at ORNL. For the more dilute feed streams, this will be derived from the initial inlet bed quadrants of the VOG test system described in Section 5.3.
2. Bed loading data (Saturation loading and incremental): This will be reported in terms of mg of I adsorbed / gm sorbent and mg of I adsorbed / gm Ag in the sorbent. These data will be collected on deep bed systems at both INL and ORNL. Ideally, the data would be collected at multiple time intervals during the course of an experiment and from multiple points along the length of the deep bed. This would provide data on the shape of the loading curve, the extent of iodine penetration (i.e., the leading edge of the MTZ) into the bed, and assuming that the bed is sufficiently long and that the initial segments achieve saturation, the length of the MTZ could be determined. All of these would be determined as a function of time and iodide concentration.
3. Desorption or physisorption data: These data are derived either from the purge phase of the TGA loading tests used to obtain the adsorption rate data or from samples taken from a deep bed test that are subjected to analysis directly upon removal and after an out-gassing period under vacuum.
4. Effluent data: Ideally these data would be derived from samples collected from the deep-bed tests described above. The desired data include the iodine concentration in the effluent, iodine speciation in the effluent, organic moieties produced in the bed, and how these change with time. If the iodine concentration in the effluent can be measured at all inlet concentrations, then the variation in DF across the bed as a function of inlet concentration can be determined. (A scoping test will be conducted this fiscal year at ORNL to examine the use of a new instrument / technique that may allow the identification and quantification of iodine species at lower concentrations than previously achieved.)
5. Iodine speciation on sorbent: Analysis of the iodine saturated and partially saturated sorbent should be examined using x-ray diffraction (XRD), energy-dispersive spectroscopy (EDS), etc., to determine the form of the captured iodine and the iodine capture sites if possible.
6. Mass Balance: For deep bed tests, closure of the mass balance is important. There is no direct measure of this class of data as it is calculated from several other terms that can be measured. For very dilute iodine concentrations, such as would be expected in the VOG, measurement of iodine effluent concentration and speciation poses significant challenges. One approach to demonstrate mass balance closure could be to conduct tests with relatively thin beds that would result in a relatively low DF (and a measurable effluent concentration). From this it should be possible to determine inlet and outlet concentrations and the loading on the bed. If this is successful, then for the cases where effluent measurements are not possible, additional emphasis will be placed on inlet and bed loads. This will be

composed of an accurate determination of the inlet amount of iodine per unit time determined with two independent methods (e.g., feed gas calculations based on temperature and vapor pressure vs mass loss from bubbler or gas cylinder certification and periodic gas samples). For the capture portion of the mass balance, this must be composed of analysis of the bed itself, either in total or highly representative subsamples. Subsamples should be taken in triplicate, with at least two being analyzed and a third completed if the initial two vary by more than 10%.

4.2 General Off-Gas Feed Composition

Feed gas concentrations: 10 ppb to 10 ppm in air

Iodine species: Iodomethane, Iodobutane, Iodododecane as a minimum. Elemental iodine will be used to provide baseline performance.

H_2O content: Dew points of 0°C and 20°C

Other off-gas constituents: None

Nominal superficial velocity: 10 m/min at 150°C calculated based on the total flow rate and the system cross-sectional area. Selected tests will be conducted at 20–30 m/min. Only for specialized tests will high gas velocities be examined as these would allow the reduction in bed diameter and should reduce any film diffusion resistances.

Bed depths: Testing will be performed using both thin and deep sorbent beds. Thin beds are used in TGA testing and as the first bed in the VOG test system. Deep beds are present in VOG test systems. The test systems are more fully described in Section 5.

4.3 Test Plans / Approaches to Answer Each of the Specific Questions

Initial answers to some of these questions can be answered relatively quickly using accelerated testing at higher iodine concentrations. However, the entire proposed test program would require 2–3 years to complete per sorbent of interest, with both INL and ORNL participating in the experimental effort.

4.3.1 Is the adsorption rate a function of hydrocarbon chain length?

This question will be addressed directly from a series of TGA tests conducted with a feed of 1 and 10 ppm and from analysis of the iodine content in Bed 1 from VOG tests conducted with 10 and 1000 ppb iodomethane and iodododecane. The initial series of tests would be conducted at a water dew point of 0°C, and this would be followed by a series conducted at a water dew point of 20°C. The 1 ppm TGA and 1000 ppb VOG allow the two methods to be compared. If the two methods show differences, then a similar series of tests will be conducted with iodobutane. If different rates are observed at the 1 and 10 ppm or 10 and 1000 ppb levels, an intermediate concentration will be run. At least half of the test conditions should be replicated. A known complication with using thin beds at low concentrations is that the initial adsorption rate may significantly reduce the gas-phase concentration. This will alter the data analysis, which for thin beds typically assumes that all particles are exposed to a constant gas-phase concentration.

4.3.2 Is the adsorption rate a function of long-chain organic iodide concentration?

This can be answered using the same series of tests as described in Section 4.3.1.

4.3.3 What is the effect of the gas velocity on the properties determined in questions 1–3?

Four selected tests from Section 4.3.1 will be repeated at a superficial velocity of 20–30 m/min. The proposed initial selected test would be 1 and 10 ppm iodomethane and 1 and 10 ppm iodododecane. These tests would be completed on both the TGA and deep-bed systems.

4.3.4 What is the saturation concentration for various long-chain organic iodides on silver-based sorbents, and does it vary with target feed species?

Data to answer this question should be available as a subset of the data collected in the TGA system as described in Section 4.3.1.

4.3.5 What is the DF over a fixed length of bed as a function of concentration and iodine species?

This question will be addressed by a series of deep bed tests conducted at both INL and ORNL. These tests will provide both complementary data and at least two replicate tests to ensure that comparable loading data are obtained in both test systems. Initial tests will be conducted at high inlet concentrations, as these are the easiest to measure the resulting DF. These tests will be conducted at a dew point of 20°C. The test columns should be designed to permit the periodic removal of small samples without significantly disturbing individual beds. Bed length should be at least 25 cm. Such a column is described in Section 5.4.2. Design should also allow periodic removal and replacement of a final bed segment that could be analyzed for breakthrough and DF determination. The proposed test sequence is as follows:

Phase 1: 5 ppm I_2, 10 ppm iodomethane, 10 ppm iodododecane, 10 ppm iodobutane

Phase 2: 500 ppb I_2, 1 ppm iodomethane, 1 ppm iodododecane, 1 ppm iodobutane

Phase 3: 5 ppb I_2, 10 ppb iodomethane, 10 ppb iodododecane, 10 ppb iodobutane

A portion of the tests needed to address this question can be coupled with the tests described in Section 4.3.1. These tests require the determination of the iodine concentration in the effluent from the deep bed.

4.3.6 If the adsorption rate changes, does the DF, bed penetration depth, and bed penetration rate change in the deep bed tests? (This is the combined effect of the results of questions 1, 2, 3, and 5.)

This would be answered by comparing the results of the tests described in Section 4.3.1–4.3.3 and 4.3.5.

4.3.7 What is the length and shape of the mass transfer zone (MTZ), and how does this vary or change for CH_3I and other organic iodides on silver-based sorbents?

This would be determined using the final set of periodic sampling of the individual segments from the tests described in Section 4.3.5 using a test column similar to the one described in Section 5.4.2.

4.3.8 Does the ratio of physisorption to chemisorption vary with chain length and concentration?

This question will be addressed by the iodine loading data from the pre- and post-purge data from the TGA system and deep-bed tests and the iodine loading data pre- and post-out-gassing under vacuum sample analysis from the VOG column quadrants. This makes use of existing samples but requires subdividing the samples for separate handling.

4.3.9 What is the resulting form of the adsorbed iodine?

This question will be addressed by the physical analysis of the post-purge samples from the TGA tests and the post-out-gassing under vacuum sample analysis from the VOG column quadrants. This makes use of existing samples but requires subdividing the samples for separate handling and analysis.

4.3.10 Is there an organic iodide concentration below which the sorbent becomes ineffective?

If material balances and DFs are accurately determined at higher concentrations, but the material balances show less recovery at lower concentrations, and actual loading on the lead segments remains relatively constant, this may be an indicator of the approach of a concentration-based rate-limiting step.

4.3.11 What is the effect of AgZ and AgAerogel on long-chain iodides, and can chemical speciation of organics and organic iodides exiting sorbent beds be determined?

This will require either the sampling of the effluent stream from the deep beds or the direct coupling of the effluent to one or more analytical instruments. An analysis system currently under development at ORNL may be suitable for the analysis of samples collected and concentrated from the effluent.

4.4 Test Plan Effort / Requirements

The testing proposed here represents a multiyear effort at both ORNL and INL (or other appropriately equipped laboratories). An estimate of project duration for each objective is provided in Table 1. In some cases, the series of tests planned will support multiple objectives, as shown in the table. The estimated durations assume that the funding levels are relatively constant. To complete a number of these objectives, the development of additional analytical methodologies will be required and is also shown. Given that iodine capture of these species could be a limiting factor in regulatory compliance for an UNF reprocessing facility, completion of this multiyear test plan could be an important component of future US off-gas R&D efforts.

Table 1. Test Plan Effort and Development Requirements.

Test Series	Expected duration (months)	Supports additional objective	Requires analytical development	Proposed analytical development time (months)
4.3.1	12–24	4.3.2, 4.3.4, 4.3.6, 4.3.8, 4.3.10	No	–
4.3.3	4–6	–	No	–
4.3.5	8–12	4.3.6, 4.3.7	Yes	8
4.3.9	6–12	–	Yes	3
4.3.10	6–12		Yes	8–12
4.3.11	6–10	–	Yes	8

5. EXPERIMENTAL MATERIALS AND TEST SYSTEMS

5.1 Experimental Materials

The AgZ is obtained from Molecular Products in an engineered 1/16-in. pellet form (Ionex-Type Ag 900 E16) containing ~10% silver by weight. The material is reduced before testing by a 10 day exposure to a H_2/N_2 gas stream at 270°C, as described in Anderson et al. (2012). The reduced AgZ (Ag^0Z) has a measured bulk density of 0.84 g/cm^3. Selected tests may also be conducted with as-received AgZ or pre-aged Ag^{0}Z to serve as bounding cases.

Silver-functionalized silica-aerogel was previously provided by Pacific Northwest National Laboratory in 100 g batches from 2014 through 2017. A description provided with the 2017 shipment reports an iodine sorption capacity of 394 mg/g. Assuming 100% silver utilization, this corresponds to a silver content of 33.5 wt%. AgAerogel, as provided, was a granular, primarily black material of nonuniform particle size with heterogeneously distributed flecks of yellow color. After extended exposure to the gas streams utilized in these experiments, the material converted to a purer black color in the absence of NOx in the feed gas stream. The sorbent turns white, followed by bright yellow at high NOx concentrations in the feed stream. The measured bulk density was 0.54 g/cm^3 for the as-received material and 0.62 g/cm^3 for the post-run material.

5.2 TGA Test System

A macro TGA system has been built and is routinely used to measure the weight changes in sorbent samples. The sample is contained in a basket suspended from a tripod. The stainless steel wire mesh basket hangs in the center of a fixed tube or chimney through which there is an upward flow of the test gases. The sample, chimney, and support are housed in an oven enclosure that provides temperature control. The tripod from which the basket is suspended is supported on a platform connected to an electronic balance located directly below the oven. The supports for the platform penetrate the oven enclosure through openings only slightly larger in diameter than the supports. Vacuum is supplied to the oven enclosure to remove gas at the same rate that it is supplied.

The TGA system is fed from a gas manifold system that allows precise control of the feed gas composition. This feed system provides (1) a dry air source (near bone-dry conditions); (2) an airstream saturated with water vapor at a controlled temperature, (3) an airstream saturated with iodine (I_2) at a controlled temperature; (4) a NO stream; (5) a NO_2/airstream; and (6) an organic iodide stream. A flow diagram is shown in Figure 1 (vacuum and NO, NO_2, and organic iodide streams are not shown).

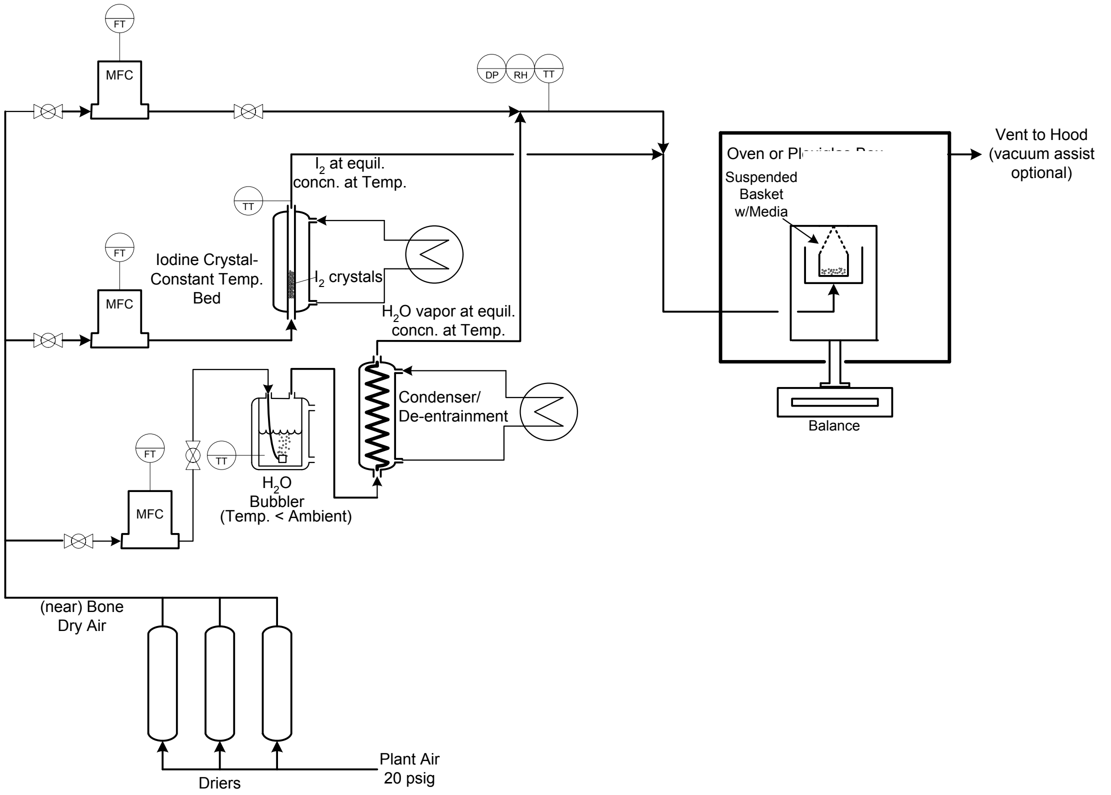

Figure 1. Flow sheet for macro TGA system.

5.3 VOG Test Systems

ORNL used three sorbent beds in series for previously reported work at low iodine concentrations. The system is described here and will be used with minimal modification for the testing proposed here. The first, Bed 1, was a thin bed with depth of ~0.25 cm segmented azimuthally into quadrants. Bed 2 was a deep bed of length ~10 cm intended to be long enough to be greater than the length of the MTZ and to capture the bulk of the iodine in the stream. The final bed was ~0.75 cm in depth and was intended to serve as a breakthrough detector. A schematic of this system is shown in Figure 2. Figure 3 shows the assembled bed system prior to installing in the oven.

The system was designed to capture multiple pieces of information in a single test. The quadrant bed could provide adsorption rate data since individual quadrants could be sampled at various times, thus allowing comparisons between sorbent material capture performance after times such as 1 day and 1 week. Prior experience at higher iodine concentrations (~50 ppm as opposed to 10–1000 ppb) in a TGA with beds of similar length has demonstrated that the capture performance of thin beds at ppm concentrations is not effective enough to sufficiently deplete the inlet stream, meaning that the concentration profile of the feed stream does not change significantly throughout the bed. As an example of this, 2 g of sorbent exposed to 50 ppm I_2 at 10 m/min total gas velocity would be expected to saturate with iodine in ~30 minutes, but a similar amount of sorbent can take up to 1–2 weeks to fully saturate at ppb concentrations. At ppb concentrations the presence of even a short initial bed could deplete the feed gas stream enough to significantly alter the makeup of the stream entering the deep bed.

Bed 2 was split into two nearly equal halves across two glass columns. Upon completion of the tests, Bed 2 could be selectively removed by vacuum into several roughly equal sections (typically eight) and analyzed to determine the sequential progress of iodine through the bed. Finally, the gas passes through Bed 3 and can be sampled intermittently and replaced online during the test to determine iodine breakthrough.

Certain engineering parameters within an adsorption system, particularly the length of the MTZ, may be functions of the gas velocity. The gas velocity for VOG testing was set to 10 m/min in a glass column of 3.45 cm diameter held at 150°C. This did not result in a turbulent flow regime, and the velocity profile could be radially uneven. This did not affect the total iodine delivery to the system but could have the effect of preferentially distributing iodine towards the center of the column. To minimize this concern, the inlet portion of Bed 1 was modified to include a mixing zone consisting of glass bead packing before the sorbent bed to ensure that the water and iodine-bearing streams mixed thoroughly and were distributed evenly to the sorbent bed.

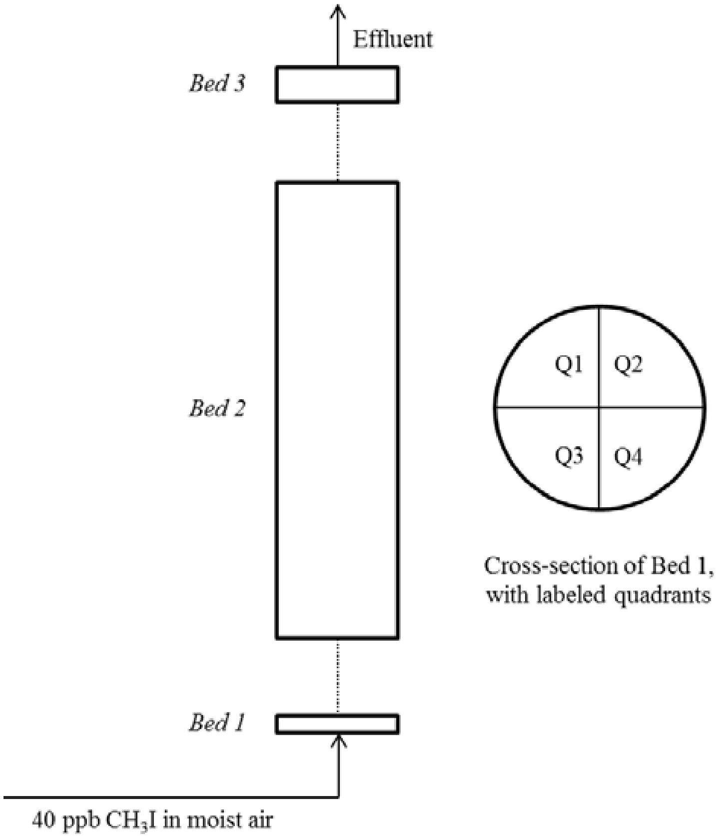

Figure 2. Schematic of test system. Feed concentration and gas can vary from 10–1000 ppb and can be either CH_3I or I_2.

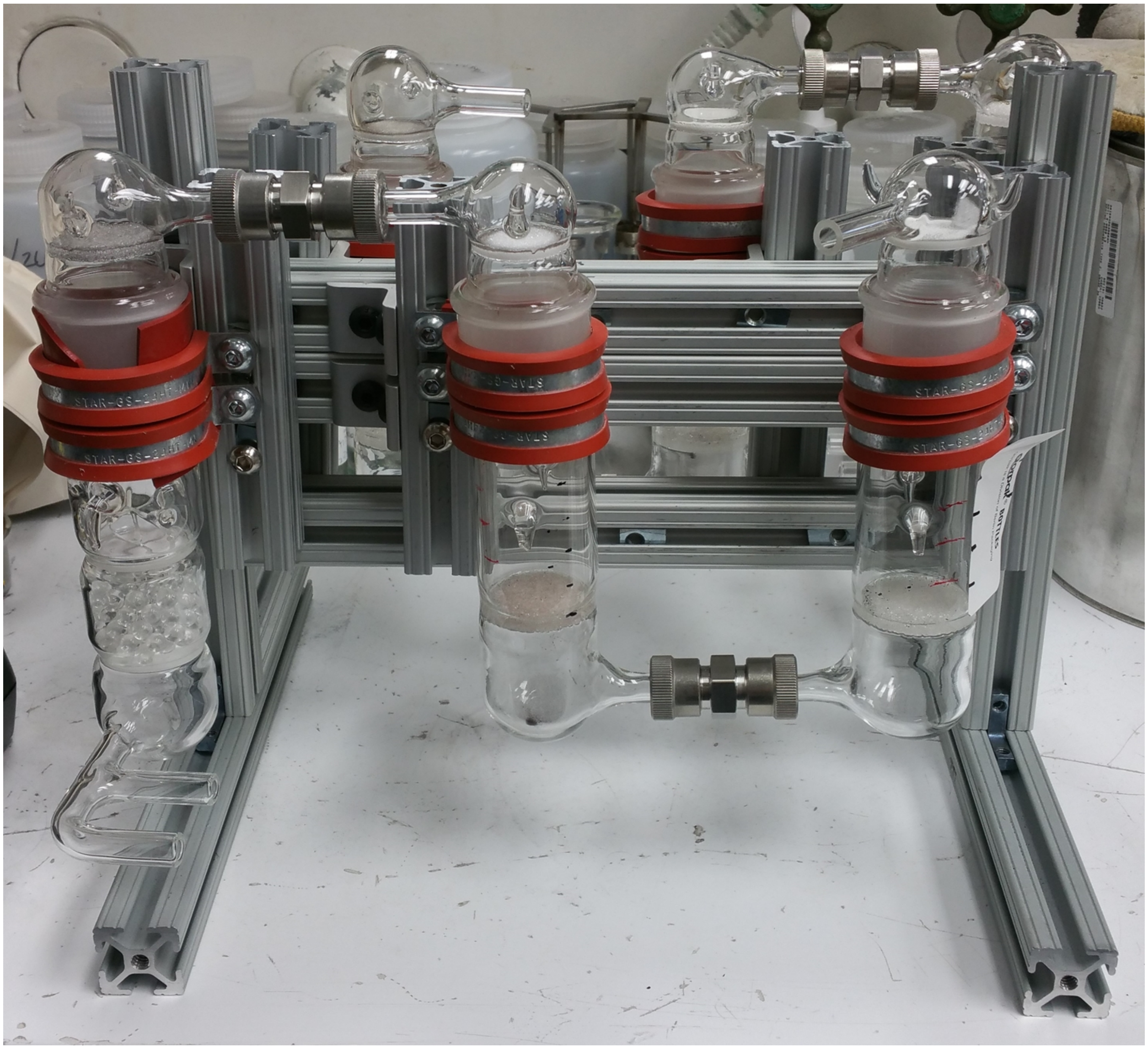

Figure 3. VOG test beds.

5.4 Deep Bed Test Systems

5.4.1 INL

The INL deep-bed iodine adsorption test system is shown in Figure 4. Variations of this test system have been used to measure iodine sorbent capacity and DF since 2008. The multiple bed design enables estimation of the depth of the MTZ. The test system consists of the following main components:

- Process gas supply and blending system, which supplies gases from gas cylinders, gas generators, and a humidifier
- Multiple sorbent bed system inside a heated oven
- Inlet and bed segment outlet gas sampling system

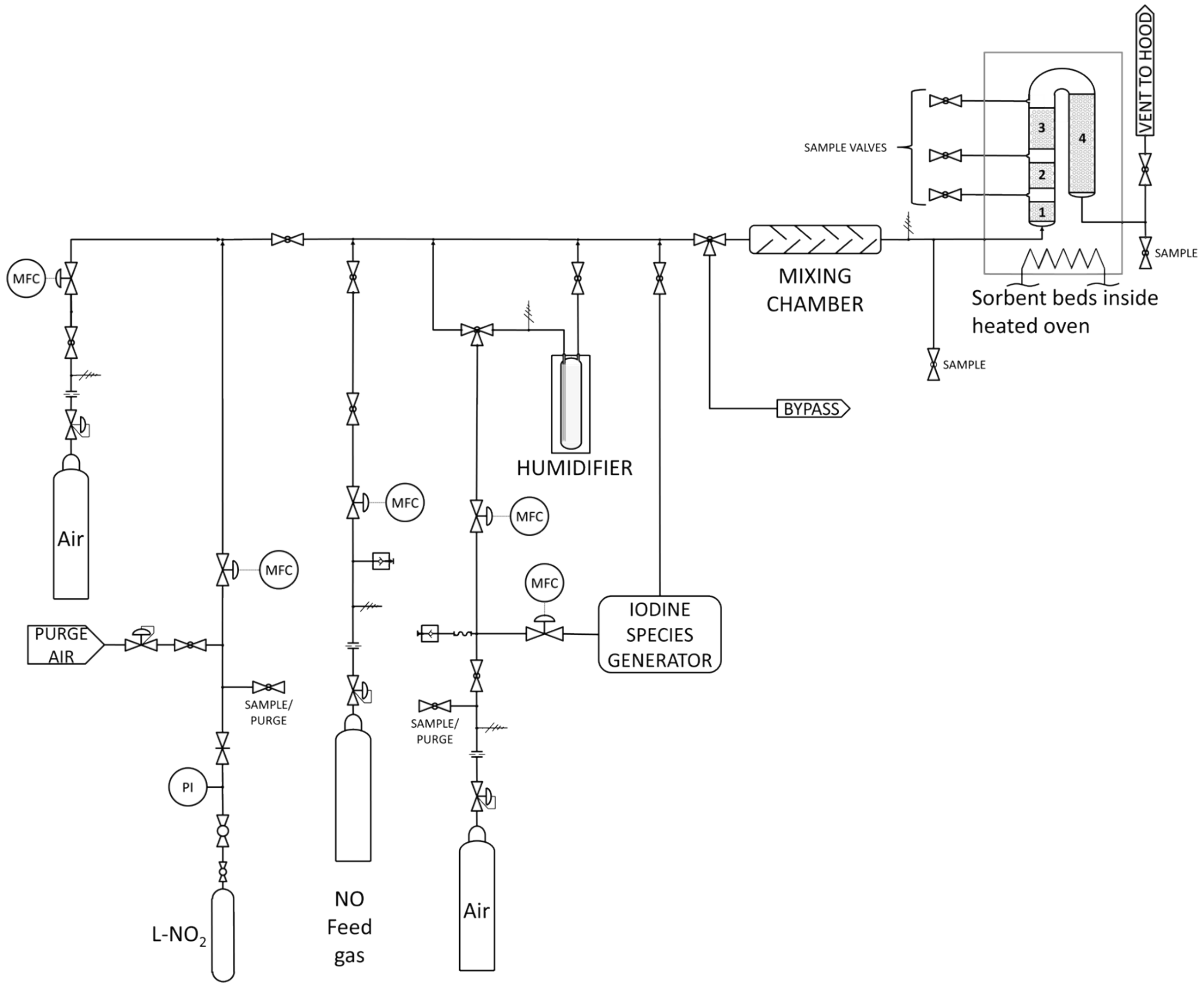

Figure 4. INL deep-bed iodine adsorption test system.

The gas supply system can provide and blend gases with varying levels of iodine species, moisture, and NO_x in either air or N_2, to emulate a variety of gas streams including DOG and VOG. Gas flow rates have typically ranged from 0.7–1.5 L/min to provide superficial gas velocities between 4–10 m/min. Iodine sources vary depending upon desired species and concentration. Permeation tubes are frequently used, but fixed bed iodine generators have also been used. Future tests with less volatile iodine species such as iodododecane may require design and use of a heated bubbler generator system.

Up to four separate “deep-bed” segments, shown loaded with AgZ following an iodine adsorption test in Figure 5, have been used. In this figure, the gas flow enters the bottom-right shallow 0.5 in. bed segment, flowing up through the first three increasingly deep segments and also up through the fourth, deepest segment. Other configurations include gas flow up through the first three beds and then down through the fourth bed.

Gas sample ports between each segment enable gas sample collection for iodine species concentrations and DF measurements. The sorbent capacities are determined if the first, shallowest beds approach saturation by analyzing the iodine concentration in the spent sorbent. Sorbent capacities are measured both gravimetrically and by a scanning electron micrograph (SEM) EDS.

Figure 5. Four “deep-bed” segments inside the oven used to maintain temperature during testing.

5.4.2 Deep bed with sampling provisions

Some testing proposed here will require the assembly of a specially designed deep bed that can allow the periodic removal of small samples at selected intermediate points within the length of the bed. The periodic sampling capability will permit (1) the identification of the leading edge of the adsorption front with time; (2) the determination of the shape of the loading curve as the adsorption progresses; (3) determination of the amount of iodine loaded on the column as a function of time, and if the column is long enough; (4) the saturation loading; and (5) the length of the MTZ.

The current concept consists of nine individual columns similar to the bed shown on the right in Figure 5. The gas flow in each segment is up-flow to allow easy removal from the trailing edge of the segment. The first two segments provide for a bed depth of 1.25 cm. Segment 3 is 2.54 cm deep, and segments 4–9 are each 5.1 cm deep. Tests will be performed with periodic sampling and with sampling only after test end. It is recognized that the periodic sampling has the potential to perturb the performance of the system, and the direct comparison of the sampled system with the one sampled only at the end will allow the impact of periodic sampling to be determined. If the effects are minimal, it may be possible to reduce the testing to a single system; otherwise, it may be necessary to perform some tests with both sampling modes.

Provisions will also be provided to allow inter-stage gas sampling (i.e., between individual beds). One concern of inter-stage sampling is the disruption of gas flow to subsequent stages.

5.5 Generation Methods for Test Gases

Three methods are proposed to generate iodine-bearing streams: a gas bubbler system for organic iodides, crystalline generator (I_2), and permeation tube within a gas generator (both organic iodides and I_2).

CH_3I can be delivered using a bubbler placing in a Stirling Shuttle freezer. This freezer can provide operating temperatures down to -80°C. Air is supplied to the bubbler using a mass flow controller (MFC). Longer chain organic iodides will require the bubblers to operate at high temperature to provide sufficient vapor pressure and evaporation rates. Heated transfer lines and /or dilution will be required to prevent condensation.

A crystalline iodine generator can be used to generate high-concentration I_2 streams (100 ppm I_2 for a total atomic iodine content of 200 ppm). The dry air to the column containing crystalline iodine maintained at 18°C is controlled by a separate MFC. Based on the vapor pressure of iodine at this temperature, the total iodine content in the feed stream can be determined. This method is known to reliably generate iodine at high concentrations based on prior work.

The final method of generation is the use of permeation tubes provided by a permeation tube vendor such as Kin-Tek Analytical or Valco Instruments Co. Inc (VICI). In this system, nitrogen or air is passed through a glass chamber containing permeation tubes that release either elemental or organic iodine at a pre-determined rate. This is then blended with other supplied gases to provide the test gas flow rate and composition. The permeation tubes will be certified by gravimetric analysis by the manufacturer before delivery; delivery rates are typically known to within 1 ng/min. The size of the on-board oven and availability of suitable permeation tubes for iodobutane and iodododecane remain to be determined. If suitable permeation tubes cannot be provided for the desired gas and the desired flow rate for some test conditions, then other gas generation methods will be required.

6. CONCLUSIONS

This document provides a short review of the penetrating forms of iodine and the results of some initial iodine capture tests under VOG conditions. It then describes a series of outstanding questions that apply to both DOG and VOG conditions and lays out a series of high-level, interrelated tests to provide insight into these questions.

7. REFERENCES

K. K. Anderson, S. H. Bruffey, D. L. Lee, R. T. Jubin, and J. F. Walker, “Iodine Loading of Partially Reduced Silver Mordenite,” FCRD-SWF-2013-000079, ORNL/LTR-2012/624, Oak Ridge National Laboratory, Oak Ridge, TN, December 28, 2012.

S. H. Bruffey, B. B. Spencer, D. M. Strachan, R. T. Jubin, Nick Soelberg, and B. J. Riley, *A Literature Survey to Identify Potentially Problematic Volatile Iodine-Bearing Species Present in Off-Gas Streams*, FCR&D-MRWFD-2015-000421, ORNL-SPR-2015/290, June 30, 2015.

D. R. Haefner and N. R. Soelberg, *Experimental Sorption Testing of Elemental Iodine on Silver Mordenite*, AFCI-SEPA-PMO-MI-DV-2009-000193, INL/EXT-09-16837, September 28, 2009.

R. Jubin, N. Soelberg, D. Strachan, and G. Ilas, “*Assessments and Options for Removal and Immobilization of Volatile Radionuclides from the Processing of Used Nuclear Fuel”*, FCR&D-SWF-2011-000305, UT-Battelle, LLC, Oak Ridge National Laboratory. 2011a.

R. T. Jubin. *“Report of the FY11 Activities of the Off-Gas Sigma Team”*, FCR&D-SWF-2011-000306, US Department of Energy Separations and Waste Forms Campaign. 2011b.

R. T. Jubin, N. R. Soelberg, D. M. Strachan, and G. Ilas, *Fuel Age Impacts on Gaseous Fission Product Capture During Separations*, FCRD-SWF-2012-000089, September 21, 2012.

R. T. Jubin, D. M. Strachan, and N. R. Soelberg, *Iodine Pathways and Off-Gas Stream Characteristics for Aqueous Reprocessing Plants – A Literature Survey and Assessment*, FCRD-SWF-2013-000308, ORNL/LTR-2013/383, INL/EXT-13-30119, September 15, 2013.

R. T. Jubin, J. A. Jordan, and S. H. Bruffey, *Performance of Silver-Exchanged Mordenite and Silver-Functionalized Silica-Aerogel Under Vessel Off-gas Conditions*, NTRD-MRWFD-2017-000034, NTRD-MRWFD-2017-000211, ORNL/SR-2017-477, 21 August, 2017a.

R. T. Jubin, S. H. Bruffey, J. A. Jordan, B. B. Spencer, N. R. Soelberg, A. K. Welty, and M. Greenhalgh, *Data Requirements and Test System Needs for Development of an Integrated Off-Gas Treatment System*, NTRD-MRWFD-2017-000422, ORNL/TM-2017-314, June 30, 2017b.

T. Nenoff, M. Rodriguez, N. Soelberg, and K. Chapman, “Silver-Mordenite for Radiologic Gas Capture from Complex Streams: Dual Catalytic CH3I Decomposition and I Confinement,” *Microporous and Mesoporous Materials*, MICMAT6530, INL/JOU-14-31276, 9 May 2014.

N. R. Soelberg, T. G. Garn, M. R. Greenhalgh, J. D. Law, R. Jubin, D. M. Strachan, and P. K. Thallapally, “Radioactive Iodine and Krypton Control for Nuclear Fuel Reprocessing Facilities,” Hindawi Publishing Corporation, *Science and Technology of Nuclear Installations*, Volume 2013, Article ID 702496, 12 pages, INL/JOU-13-28481, February 19, 2013, http://dx.doi.org/10.1155/2013/702496.