INL/EXT-12-26522

Deep Bed Adsorption Testing Using Silver-Functionalized Aerogel

Nick Soelberg
Tony Watson

June 2012

The INL is a U.S. Department of Energy National Laboratory
operated by Battelle Energy Alliance

INL/EXT-12-26522
FCRD-SWF-2012-000173

Deep Bed Adsorption Testing Using Silver-Functionalized Aerogel

Nick Soelberg
Tony Watson

June 2012

Idaho National Laboratory
Fuel Cycle Research & Development
Idaho Falls, Idaho 83415

http://www.inl.gov

Prepared for the
U.S. Department of Energy
Office of Nuclear Energy
Under DOE Idaho Operations Office
Contract DE-AC07-05ID14517

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.

ACKNOWLEDGEMENTS

We acknowledge others who helped guide or perform iodine sorption testing this year. Jack Law of the Idaho National Laboratory (INL) Aqueous Separations and Radiochemistry Department and the Department of Energy Fuel Cycle Research and Development Program Separations and Waste Forms Campaign, and Bob Jubin of the Oak Ridge National Laboratory (ORNL), and the leader of the Separations and Waste Forms Campaign Off-gas Sigma Team, provided programmatic and technical direction. Joseph Matyas of Pacific Northwest National Laboratory provided the silver-functionalized Aerogel that was tested.

Veronica Rutledge of the INL Aqueous Separations and Radiochemistry Department helped in test planning. Duane Ball and others in the INL Chemistry and Radiation Measurement Department performed iodine sample analyses. Daren Jensen provided quality assurance guidance.

This page blank

SUMMARY

Nuclear fission results in the production of fission products and activation products, some of which tend to be volatile during used fuel reprocessing and evolve in gaseous species into the reprocessing facility off-gas systems. Analyses have shown that I-129, due to its radioactivity, high potential mobility in the environment, and high longevity (half life of 15.7 million years), can require control efficiencies of up to 1,000x or higher to meet regulatory emission limits. Rightly so, the control of iodine emissions during used fuel reprocessing is an important issue. The Department of Energy (DOE) Fuel Cycle Research and Development (FCRD) Program has supported research and development on iodine control and iodine waste forms for the past several years. Iodine capture is an important aspect of the Separations and Waste Forms Campaign Off-gas Sigma Team (Jubin 2011, Pantano 2011).

Deep-bed iodine sorption testing has a unique and important role in the Off-gas Sigma Team iodine research program. The deep bed testing can:

- Measure sorbent performance under more life-like (but admittedly still idealized) sorption configurations and operating conditions
- Measure sorption efficiencies
- Measure capacity of sorbents up to breakthrough
- Estimate mass transfer zone depths
- Generate data for isotherms and dynamic modeling
- Produce greater-than-gram-quantities of iodine-laden sorbent for confirming Ag and iodine loadings and waste form studies.

The objectives of the fiscal year (FY) 2012 deep bed iodine sorbent testing are:

- Perform deep bed adsorption testing using silver functionalized aerogel
- Provide sorption data for iodine and methyl iodine dynamic sorption modeling on AgZ
- Support Systems studies performed by the Off-gas Sigma Team.

Two Aerogel sorption tests have been performed this fiscal year. Additional tests are still in progress and can be reported in a revision of this report or a future report. The silver-functionalized Aerogel sorbent was prepared and provided by Pacific Northwest National Laboratory (PNNL).

The inlet iodine concentration in Test AG-1 averaged 2.0 ppm. The inlet iodine concentration in Test Ag-2 averaged 34 ppm.

Iodine loadings on the sorbent were calculated two ways. The first way is to use the weight change of the sorbent after the test to estimate the amount of sorbed iodine, assuming that this mass change is due to only sorption of iodine. The other method uses the inlet and outlet off-gas measurements and the test duration. This method provides the ability to track iodine sorption as the test progresses. Silver utilization was also determined based on the amount of the initial silver in the sorbent that has reacted with iodine according to the stoichiometry Ag + I = AgI.

Using the gas-phase iodine measurements, the maximum iodine decontamination factor (DF) was measured to be over 10,000, above the 1,000-10,000 target DF range (Jubin 2012). The mass transfer zone may be as short as 0.5 inches under the sorption conditions of the first test.

After each test, the sorbent beds are purged with pure N_2 to desorb any amounts of iodine that may be physisorbed. Only a small fraction of the iodine sorbed on Bed 1 was desorbed during the purge periods. This indicates that, in a full-scale process, as long as the full depth of a sorbent bed is not saturated, the remaining unsaturated sorbent can serve as a “getter” for physisorbed iodine that may slowly desorb from

saturated sorbent pellets. The end result might possibly be efficient retention of the physisorbed iodine as it migrates from physisorption sites into sites where the iodine can chemisorb via reaction with the silver.

The silver-functionalized Aerogel appears to have potential to be a very effective and efficient iodine sorbent.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

BET	Brunauer, Emmett, and Teller
DF	decontamination factors
DOE	Department of Energy
FCRD	Fuel Cycle Research and Development
FP	fission products
FY	fiscal year
GC	gas chromatograph
INL	Idaho National Laboratory
ICP-MS	inductively coupled plasma mass spectrometry
MS	mass spectrometry
MTZ	mass transfer zone
ORNL	Oak Ridge National Laboratory

This page blank

1. INTRODUCTION

Nuclear fission results in the production of fission products and activation products that increasingly interfere with the fission process as their concentrations increase. If used nuclear fuel is reprocessed, volatile radionuclides including I-129 would evolve into the process off-gas systems and could require off-gas control to limit air emissions to levels within acceptable emission limits.

Analyses show that I-129, due to its radioactivity, high potential mobility in the environment, and high longevity (half life of 15.7 million years), can require control efficiencies of up to 1,000x or higher to meet regulatory emission limits (Soelberg 2008, Jubin 2012).

1.1 Role of Deep Bed Testing

The control of iodine emissions during used fuel reprocessing is an important issue. The Department of Energy (DOE) Fuel Cycle Research and Development (FCRD) Program has supported research and development on iodine control and iodine waste forms for the past several years. The Offgas Sigma Team was formed in 2009 within the Separations and Waste Forms Campaign to establish a team of researchers from different DOE sites to focus on research and development for emissions control and waste forms for volatile radionuclides. Figure 1-1 shows iodine control and waste form research areas and interfaces within the Off-gas Sigma Team. Deep-bed iodine sorption testing has a unique and important role in the Off-gas Sigma Team iodine research program, recognized in the Fiscal Year (FY) 2011 Off-gas Sigma Team Peer Review (Pantano 2011). The deep bed testing can:

- Measure sorbent performance under more life-like (but admittedly still idealized) sorption configurations and operating conditions
- Measure sorption efficiencies
- Measure capacity of sorbents up to breakthrough
- Estimate mass transfer zone depths
- Generate data for isotherms and dynamic modeling
- Produce >gram-quantities of iodine-laden sorbent for confirming Ag and iodine loadings and waste form studies

1.2 Summary of Pre-2012 Deep Bed Test Results

Deep-bed iodine sorbent testing was started at the INL in the year 2009 and has continued through this year (Haefner 2009, Haefner 2010, Soelberg 2011). Accomplishments prior to FY 2011 include:

- Design and build bench-scale test system
- Developed and applied analytical techniques
    - Resolved handling techniques to prevent contamination, enabling decontamination factor measurement of up to 10,000x depending on variations in measured values and detection limits
- Initial tests showed iodine DFs of 1,000 – 10,000, exceeding target levels (100-1,000)
- Used diatomic iodine in initial tests; added methyl iodide in year 2

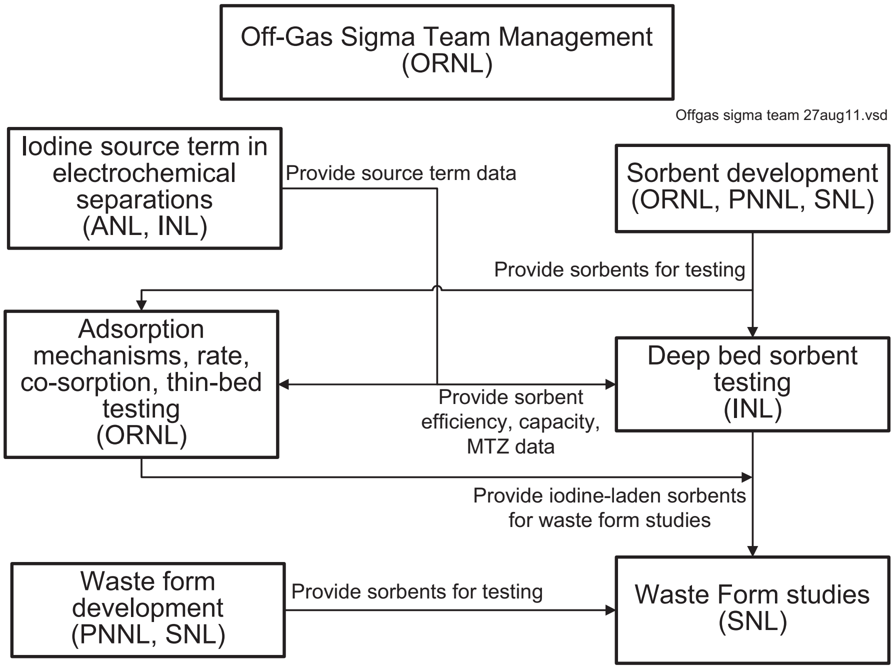


Figure 1-1. Iodine control and waste form research and development interfaces within the Off-Gas Sigma Team.

- Showed that (under test conditions) the order of magnitude of DFs was not significantly affected by the gas matrix (H_2O, NO_x, and N_2 (versus air)
    - Data was not yet sufficient to determine if capacity or mass transfer zone (MTZ) are impacted, or if smaller (+/-10%) impacts on DFs occur from gas matrix effects, especially under longer actual operation
    - Initially tested sorbents were all Ag mordenites – IONEX AG900 procured commercially and silver-reduced Ag mordenite from Oak Ridge National Laboratory (ORNL).
    - Testing in 2011 expanded to include other sorbents, when the NC-77 sorbent from Sandia National Laboratory was tested.

1.3 Remaining Issues and Data Gaps

While the understanding of iodine sorbent performance has progressed under the Off-gas Sigma team focus, some issues and data gaps remain. These include:

- Understanding of adsorption mechanisms
- Performance information (control efficiency, capacity, MTZ, etc.) for novel new sorbents
- Data gaps such as isotherm data for previously tested sorbents
- Data for dynamic iodine sorption modeling
- Waste form performance data, incorporating the conversion or use of the iodine sorbent in the waste form

The need for continued deep bed iodine sorption testing to help address these was emphasized by the FY 2011 Sigma Team (Pantano 2011): "We strongly support the study on iodine capture on deep beds."

1.4 Objectives and Scope of FY 2012 Deep Bed Testing

The objectives of the FY 2012 deep bed iodine sorbent testing are:

- Perform deep bed adsorption testing using silver functionalized aerogel
- Provide sorption data for iodine and methyl iodine dynamic sorption modeling on AgZ
- Support Systems studies performed by the Off-gas Sigma Team.

A test plan was prepared in early FY 2012 (Soelberg 2011), and has been the guiding document for work performed this year. Tests were generally performed for a long enough duration so that breakthrough occurred. These breakthrough tests enabled the determination of sorption efficiencies up to the time of breakthrough, and sorbent capacities at the time of breakthrough (which is the practical limit to the sorbent capacity, even though sorption is expected to continue in the "spent" sorbent after breakthrough). All work was performed in compliance to work control documentation that was updated for this year's work, to ensure data quality, worker safety, environmental protection, and regulatory compliance during testing (INL 2011).

The tests were designed to primarily demonstrate the sorbent performance for capturing iodine species in hypothetical aqueous dissolver off-gas, recognizing that a variety of other gas streams could exist in an aqueous separations process; some of which would have considerably different compositions and flowrates (Figure 1-2).

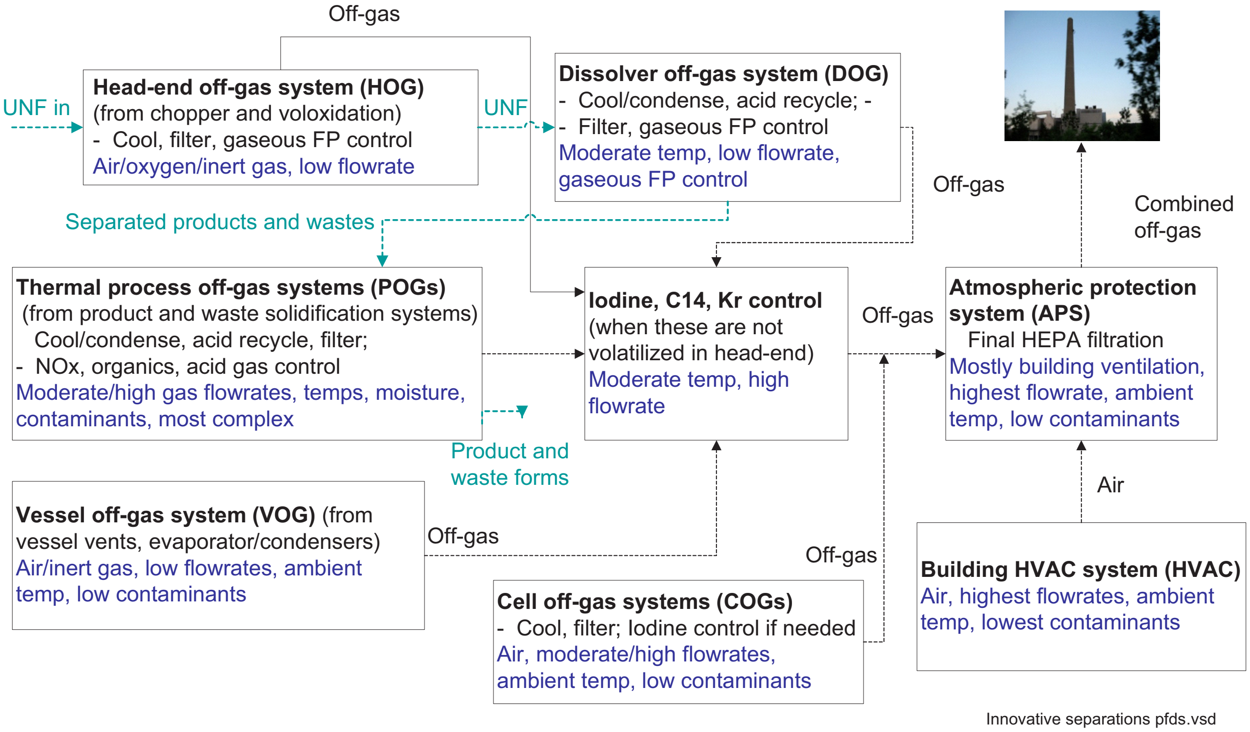


Figure 1-2. Illustration of potential off-gas streams from an aqueous separations plant.

Tests proceeded to the extent of available funding and time. Not included in the scope of this year's testing were:

- Tests designed to measure iodine sorption and sorbent performance for most separations process gas streams besides the dissolver off-gas

- Tests for evaluating iodine capture and sorbent performance for gas streams from electrochemical processing.

2. DEEP BED IODINE SORBENT TEST SYSTEM

Figure 2-1 shows a process diagram for the iodine test system. The main components are:

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

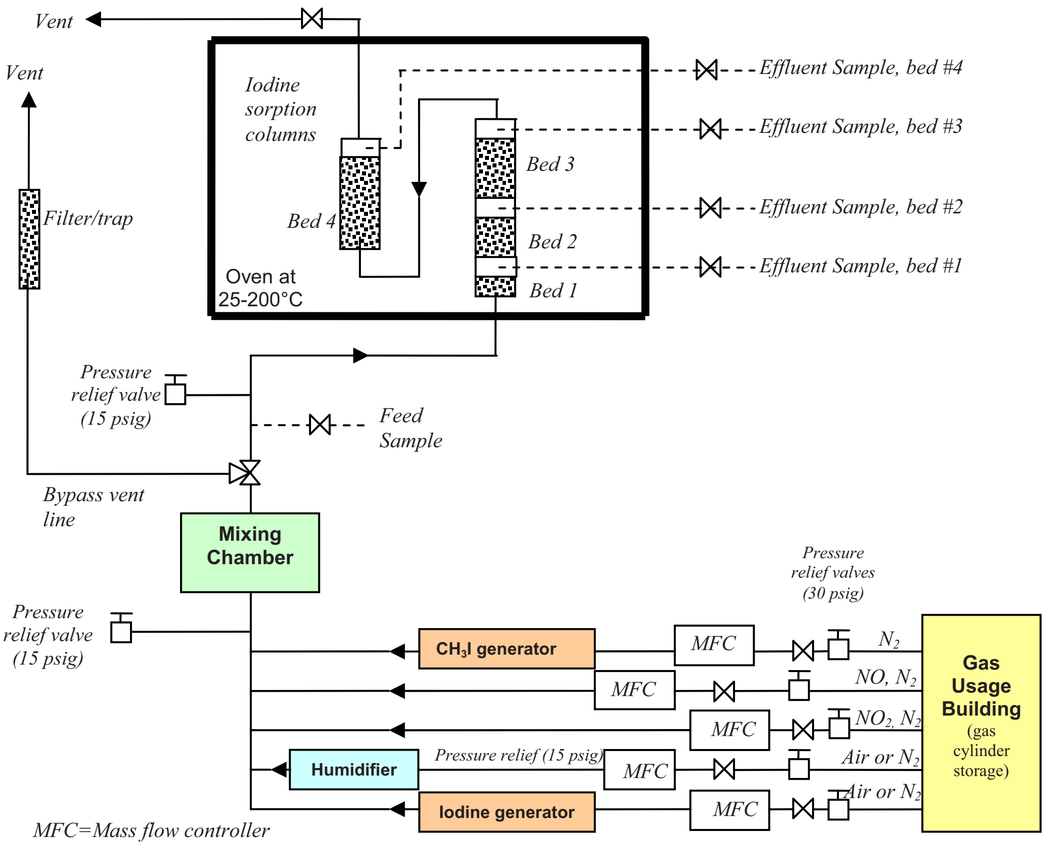


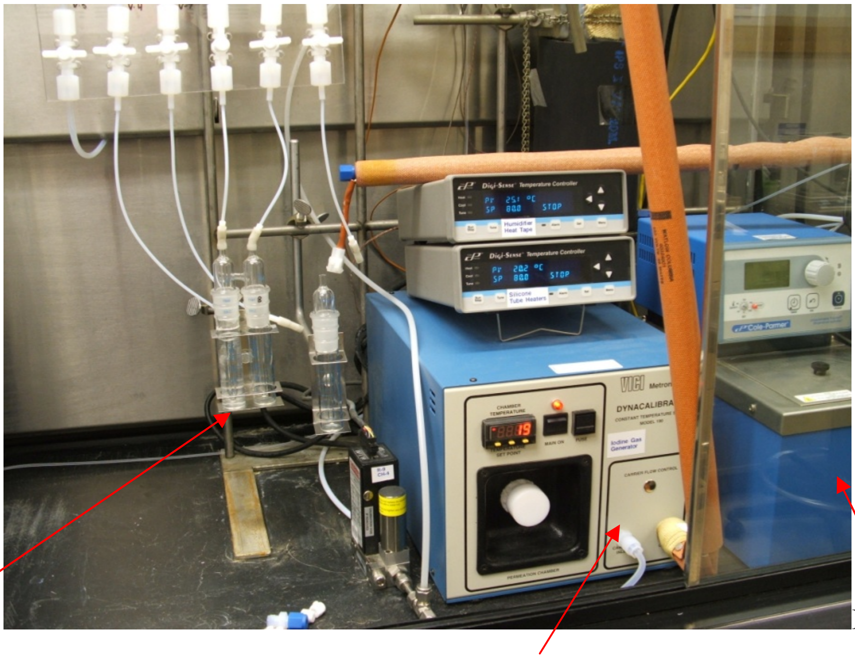
Figure 2-1. Iodine sorbent test system.

2.1 Process Gas Supply System

The process gas supply system consists of pressurized gas cylinders that supply pure air, nitrogen, NO_x, and other gases, iodine and methyl iodide generators, and a humidifier that supplies vaporized water. Air or N_2 can be supplied through mass flow controllers separately to the iodine and methyl iodide generators and the humidifier. NO and NO_2 gases, with balance N_2, are supplied from compressed gas cylinders through mass flow controllers. The gas flowrates and the generation rates of vaporized iodine, methyl iodide, and water are set to achieve the target blended gas composition and blended in a mixing chamber upstream of the sorbent beds. All process lines that contain vaporized iodine, methyl iodide, or water are electrically heat traced.

2.1.1 Iodine Generator

Three versions of iodine generators have been tested and used in this year or prior years. When low concentrations of iodine, below about 1 ppmv in the blended gas, are desired, then iodine can be generated using a permeation tube system. Permeation tubes contain solid iodine crystals in semi-permeable tubes. The tubes emit a known flowrate of iodine at a constant rate which is controlled by the operating temperature of the tube. The tubes (up to two), from VICI Metronics, are placed inside a Dynacalibrator Model 190 constant temperature permeation tube system (shown in Figure 2-2) also from VICI Metronics.



I2 bubblers

Fixed bed I_2 generator

Permeation tube I_2 or CH3I generator

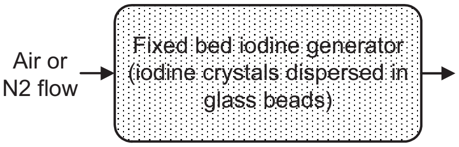
Figure 2-2. View of the iodine bubblers, the permeation tube iodine or methyl iodide generator, and the humidifier.

The VICI Metronics permeation tube system cannot operate at temperatures above 110°C, the upper limit that the materials of construction can tolerate. The maximum iodine concentration that can be supplied from a maximum of two permeation tubes at this temperature is about 1 ppmv in the blended gas mixtures at a total gas flowrate of about 1.5-2 l/min, the flowrate needed to provide the desired superficial gas velocities in the sorbent beds of up to 10 m/min, in the target range of sorbent operating temperatures of about 25-150°C. For higher iodine flowrates, three types of fixed bed iodine generators were tested, before the third was found to be most acceptable.

Figure 2-3 shows the third generation iodine generator, which was tested and found to be superior to the other two versions. In this version, iodine crystals were mixed with glass beads and placed inside the Teflon vessel. The iodine crystals are distributed among the glass beads, which reduces the tendency of the crystals to clump together. This design, although it still did not provide the maximum flowrate expected if the sublimation process was in thermodynamic solid-gas equilibrium, provided the most constant flowrate. The iodine flowrate and concentration in the blended gas stream was measured periodically whenever the bed outlet iodine concentrations were measured.

A. Single bed of iodine crystals that tended to clump together and reduce iodine ablation rate.

B. Iodine crystals inside a bundle of Teflon tubing; clumping was reduced.



Offgas sigma team 27aug11.vsd

C. Single bed of iodine crystals dispersed in glass beads; provided most constant and controllable iodine flowrate for higher iodine gas flowrates.

Figure 2-3. First, second, and third generation iodine generators for high iodine flowrates.

2.1.2 Methyl Iodide Generator

Methyl iodide was also provided two different ways. For low concentrations (under about 1 ppmv in the blended gas), methyl iodide can be provided from a certified compressed gas cylinder containing up to about 100 ppm methyl iodide. This was the methyl iodide delivery method used in FY 2010 testing when lower concentrations were used.

For higher methyl iodide concentrations (above about 1 ppmv in the blended gas), it becomes increasingly impractical and costly to use methyl iodide supplied in gas cylinders. In these cases, methyl iodide permeation tubes from VICI Metronics were used in the permeation tube system to provide methyl iodide at concentrations up to about 50 ppmv. The higher concentrations of methyl iodide from the permeation tubes were possible (compared to the highest possible iodine concentrations from iodine permeation tubes) because the methyl iodide tubes had higher specific sublimation rates at lower temperatures.

2.1.3 Humidifier

Humidified air was produced by passing air or nitrogen through a fritted glass bubbler submerged in a constant temperature bath. A thermocouple in the headspace of the bubbler provided the temperature of the water-saturated gas. The concentration of water in the blended gas was controlled by adjusting the gas flowrate through the humidifier and the humidifier operating temperature.

2.2 Sorbent Bed Segments

Figures 2-4 and 2-5 show detail of the sorbent beds and how the sorbent beds are configured in a temperature-controlled oven.

2.3 Sample Collection and Analysis

Iodine and methyl iodide concentrations in the process gas can be measured at up to five locations in the test system – at the inlet to the sorbent bed segments, and at the outlet of each of the four bed segments. Since the gas flowrate is essentially the same at all five sample locations, the removal efficiencies for the sorbent in all four beds can be determined by measuring the iodine and methyl iodide concentrations at these locations. By integrating over time and using the process flowrate, the amounts of iodine and methyl iodide sorbed on each of the beds can be calculated.

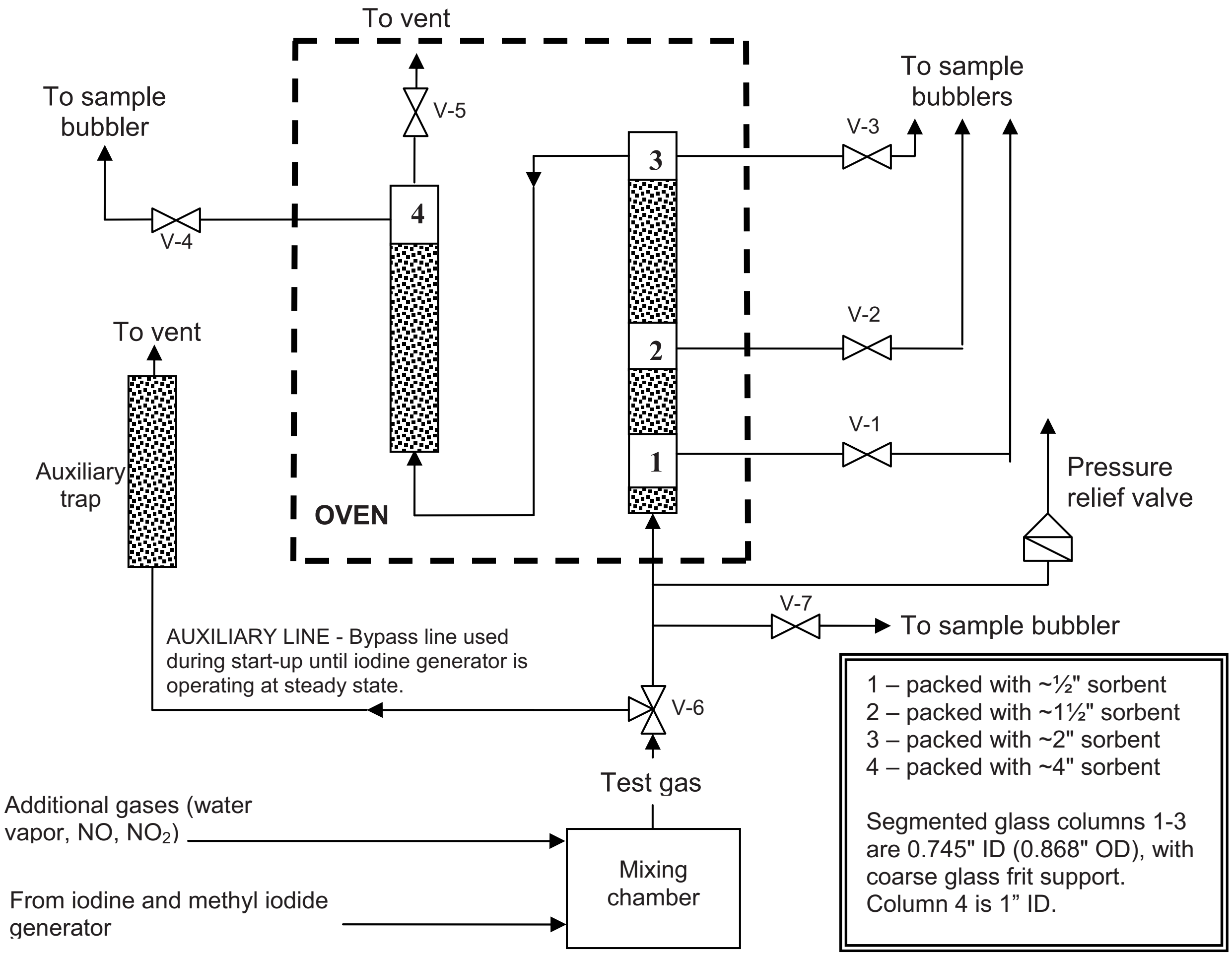


Figure 2-4. Detail of the sorbent beds. At times, only 3 instead of all 4 beds are used.

2.3.1 Iodine Sample Collection and Analysis

For measuring the gaseous iodine concentration, the process gas from any of the five sample locations is passed through 25-ml "midget" impingers (shown in Figure 2-2 above) that contain 0.1 N NaOH for scrubbing halogen gases including I_2 and HI, if present. This technique is modeled after EPA Method 26 "Determination of Hydrogen Halide and Halogen Emissions from Stationary Sources, Non-Isokinetic Method" (40 CFR 60 Appendix A). The caustic solution dissolves halogens by hydrolyzing halogen gases to form a proton (H^+) and hypohalous acid. Any HI, if present, dissolves by dissociating in the caustic solution, and is included with I_2 in the analysis.

The typical NaOH concentration in the 25-ml bubblers has been 0.1 N, as specified in Method 26. This provides orders-of-magnitude safety factor in the absorbing capacity of the solution. We occasionally check the pH of the bubbler solutions to verify that the absorbing capability of the solution is not depleted.

The bubbler solutions are analyzed by inductively coupled plasma mass spectrometry (ICP-MS) per EPA Method 6020A (SW-846, "Test Methods for Evaluating Solid Wastes Physical/Chemical Methods," http://www.epa.gov/osw/hazard/testmethods/sw846/online/). We can detect gaseous iodine concentrations as low as 0.08 ppbv with this method. Higher concentration samples for gas streams with 1 ppmv or higher iodine concentrations are typically diluted for analysis.

Figure 2-5. Configuration of the sorbent beds inside the temperature-controlled oven.

2.3.2 Methyl Iodide Sampling and Analysis

Methyl iodide was not used in Aerogel tests performed up to the date of this report, because the gas chromatograph (GC) used to speciate the methyl iodide was malfunctioning after several troubleshooting and repair attempts. It is possible that the corrosive iodine sorption test process gas streams, that, at times, contains I_2, CH_3I, and NO_x, has damaged one or more of the GC components. We are presently addressing if this GC is repairable or if a new GC is required, and how to obtain funds for that purchase.

2.3.3 Sampling and Analysis Lessons Learned

Some sampling and analysis lessons have been learned this past year and in prior years:

- When control efficiencies in excess of 1,000x are measured, then the iodine species concentrations in the process gas vary by more than 1,000x. This means that lab equipment such as bubblers, fittings, and tubing that contacts the higher-concentration gas streams and scrubber solutions can often be contaminated with iodine species at levels that are not easily removed without thorough cleaning. So we have labeled and kept separate, impingers and fittings used at each of the 5 potential sample locations. Even with multiple rinsing, if impingers used at the higher-concentration-locations are used in subsequent sample collection at the lower-concentration-locations, they can result in high-biased results due to contamination.
- The blended gas streams can corrode fittings, tubing, and equipment. The system components must be heated to above dewpoint temperatures to avoid corrosive condensation. System components, in particular for the GC and MS systems, need to be routinely cleaned, maintained, and replaced when necessary.
- Best test results are obtained when sets of samples are collected for analysis at the same time. Each set needs to include the sorbent bed inlet sample and outlet samples from each of the sorbent bed segments. Some variation or drift can occur in the inlet concentrations; obtaining a

sample of the inlet gas at the same time the sorbent bed outlet samples are obtained, provides tracking of the inlet gas concentrations should they drift over time.

- Sorbent bed breakthrough tests sometimes require 10's or 100's of hours. Sample periods may be extended to once every 4 hours or more in such cases to minimize sampling and analysis costs.
- On-line mass spectrometry analysis. We evaluated an on-line mass spectrometer during FY 12 for I_2, CH_3I, and HI analyses, as an alternative to the GC. We found that the mass spectrometer did not provide sufficiently low detection limits.
- We also evaluated during FY- 12, bubbler methods to capture and speciate organic iodide species. We found no methods that did not require considerable method development, which was outside the scope of this year's testing.

3. INITIAL TESTING ACTIVITIES AND EQUIPMENT MAINTENANCE

Initial activities in the fiscal year addressed some questions identified in prior testing:

- We developed a test plan that included activities to address questions from prior testing and to be a guide for additional testing (Soelberg 2011). Additional testing focused on (a) additional sorbents, (b) higher iodine concentrations (high enough to reduce the expected test time to reach breakthrough), and (c) somewhat higher gas velocities more typical of full-scale operation.
- We implemented work control requirements, documentation, and back-up temperature-control to enable extended duration operation that is sometimes needed for testing sorbents long enough to reach breakthrough.
- We evaluated an on-line mass spectrometer during for I_2, CH_3I, and HI analyses, as an alternative to the GC. We found that the mass spectrometer did not provide sufficiently low detection limits.
- We also evaluated bubbler methods to capture and speciate organic iodide species. We found no methods that did not require considerable method development, which was outside the scope of this year’s testing.
- We procured the necessary process gases.
- We performed annual maintenance on the test system, which included leak testing and background iodine testing. Suspect components were repaired or replaced. Blank testing confirmed that the test system and test equipment had low background iodine levels.

This page blank

4. DEEP BED AEROGEL TEST RESULTS

Table 1-1 lists the two Aerogel sorption tests that have been performed this fiscal year. Additional tests are still in progress and can be reported in a revision of this report or a future report. Testing was somewhat delayed and limited this year due to initial activities summarized in Section 3, and due to trouble-shooting and maintenance for the on-line GC.

The inlet iodine concentration in Test AG-1 averaged 2.0 ppm. The inlet iodine concentration in Test AG-2 averaged 34 ppm.

Table 4-1. Sorption test results using silver-functionalized Aerogel.

Run Number	Test AG-1			Test AG-2		
Simulate what off-gas?	dissolver			dissolver		
Test dates	6 Mar 12 to 4 Apr 12			23 May to 31 May 12		
wt% silver	30%			30%		
Pretest mass, Bed 1, g	2.13			2.10		
Pretest mass, Bed 2, g	6.4			6.58		
Pretest mass, Bed 3, g	8.34			9.20		
Pretest mass, Bed 4, g	26.78			0.00		
Pretest total mass, Total, g	43.65			17.88		
Post-test mass, Bed 1, g	2.37			2.45		
Post-test mass, Bed 2, g	6.53			7.48		
Post-test mass, Bed 3, g	8.02			9.57		
Post-test mass, Bed 4, g	27.53	Iodine loading and Ag utilization from weight gain		0.00	Iodine loading and Ag utilization from weight gain	
Post-test total mass, Total, g	44.45	Loading, wt%	Ag utlization, %	19.50	Loading, wt%	Ag utlization, %
delta mass, Bed 1, g	0.24	11%	32%	0.35	17%	47%
delta mass, Bed 2, g	0.13	2.0%	0.8%	0.90	14%	39%
delta mass, Bed 3, g	-0.32	---	---	0.37	4.0%	11%
delta mass, Bed 4, g	0.75	2.8%	0.3%	0.00	---	---
delta mass, total, g	0.8	---	---	1.62	---	---
I2 fixed bed system	Ag utilazation is calculated assuming AgI chemical formula					
Water bath T, deg. C	27			45		
Carrier gas type	N2			N2		
Carrier gas rate, sccm	9			150		
I2 conc., ppm	367			361		
% of I2 saturation level	60.0%			15.0%		
Make-up gas system						
Gas type	N2			N2		
Gas rate, sccm	880			740		
Humidifier system						
Humidifer oven T, deg. C	31.0			31.0		
Humidifier oven P, inches Hg	25.5			25.5		
Humidifier saturation efficiency, %	95%			95%		
Carrier gas type	N2			N2		
Carrier gas rate, sccm	500			500		
Carrier gas moisture content, vol %H2O	4.8			4.8		
Total gas flowrate	525			525		
Other gases						
NO ppmv	10,000			10,000		
NO2 ppmv	10,000			10,000		
NO gas rate, sccm	135			135		
NO2 gas rate, sccm	135			135		

Table 4-1 (continued). Sorption test results using silver-functionalized Aerogel.

Run Number	Test AG-1	Test AG-2
Sorption conditions		
Temperature, deg. C	150	150
Total gas flowrate, sccm	1,684	1,685
Target I2 conc, ppmv	2.0	32
Measured I2 conc, ppmv	2.0	34
Target CH3I conc, ppmv	0	0
Measured CH3I conc, ppmv	0	0
Measured total I flowrate, mg/min	0.035	0.60
Measured dP all beds, in. H2O	NM	NM
H2O conc, %	1.5	1.5
H2O dewpoint, deg. C	11	11
NO conc, ppmv	801	801
NO2 conc, ppmv	801	801
Balance	N2	N2
Sorption gas velocity, f/min	10.0	10.0
Bed 1 out residence t, sec	0.076	0.076
Bed 2 out cumulative residence t, sec	0.31	0.30
Bed 3 out cumulative residence t, sec	0.61	0.61
Bed 4 out cumulative residence t, sec	1.22	1.22
Cumulative test duration, hr	242	64
Final iodine loading on Bed 1, wt%	12%	22%
Final iodine loading on Bed 2, wt%	4.1%	20%
Final silver utilization, mole %, Bed 1	35%	63%
Final silver utilization, mole %, Bed 2	12%	56%

[iodine data 21june12.xlsx]2012 aerogel test summary

4.1 Aerogel Sorbent

The silver-functionalized Aerogel sorbent was prepared and provided by Pacific Northwest National Laboratory (PNNL). Aerogel is a highly porous solid material produced by replacing the liquid component of a gel (typically silica gel) with a gas. Aerogels have low densities and high surface areas. The silica Aerogel provided by PNNL was functionalized with silver nanoparticles that were produced by reducing the silver thiolate adduct ions at 165°C for 2 h under flowing 2.7% H_2 in Ar. The Brunauer, Emmett, and Teller (BET) surface area is about 200 m^2/g. The bulk density is about 500 kg/m^3. The silver content is estimated at 30 wt% (30 g silver per 100 gm silver-functionalized Aerogel). Fresh sorbent is loaded in the three (or four, if four) sorbent bed sections prior to a test.

4.2 Test AG-1 Iodine Sorption Results

Iodine loadings on the sorbent were calculated two ways. The first way is to use the weight change of the sorbent after the test to estimate the amount of sorbed iodine, assuming that this mass change is due to only sorption of iodine. Using this method, beds 1 and 2 gained 11 wt% iodine and 2.0% iodine, respectively. The other method uses the inlet and outlet off-gas measurements and the test duration. This method provides the ability to track iodine sorption as the test progresses. Using this method, the test-end iodine sorption in beds 1 and 2 was determined to be 12% and 4.1% of the initial bed mass. Using this method, silver utilization was calculated to be 35% in Bed 1 and 12% in Bed 2. Silver utilization is defined to be the amount of the initial silver in the sorbent that has reacted with iodine according to the stoichiometry Ag + I = AgI.

Using the gas-phase iodine measurements, the maximum iodine decontamination factor (DF) was measured to be about 4,000 in the 0.5-inch deep Bed 1, and on the order of 10,000 in Beds 2 and 3.

Process gas was sampled periodically during the duration of each test to enable determination of bed inlet and outlet iodine concentrations and sorption efficiencies as each test progresses. Figure 4-1 shows the trend in gaseous iodine concentrations, decontamination factors (DFs), and silver utilization on Bed 1 during the 242-hr Test AG-1. This figure shows that:

- The initial Bed 1 DF was about 4,000 (about ½ of the DFs observed for Beds 2 and 3), and the Bed 1 DF rapidly dropped within the first 5 hours of the test. This indicates that, under the test conditions, the mass transfer zone was at least 0.5 inches deep.
- Iodine DFs in Beds 2 and 3 generally ranged around 10,000 for most of the test. Variation occurs in the Bed 2 and 3 DFs because these DFs depend largely on bed outlet iodine levels that are at or near the detection limits, so some data scatter was observed. The Bed 2 DF began to consistently drop below 10,000 after about hour 200, suggesting that breakthrough has occurred. The long time it took for consistent breakthrough of Bed 2 to occur indicates that the mass transfer zone is less than that the total bed 1 + 2 depth of 2 inches. Bed 3 breakthrough was not observed during the duration of this test, so the mass transfer zone did not progress beyond the cumulative bed 1 + 2 + 3 depth of 4 inches during this test.
- According to the Bed 1 outlet iodine measurements, the Bed 1 appears to have gradually approached saturation during this test duration. The Bed 1 outlet iodine concentration was relatively flat and nearly the same as the inlet iodine concentration for about the last 40 hrs of the test.
- Beds 2 and 3 did not reach saturation during this test, even though breakthrough appears to have occurred in Bed 2.

After each test, the sorbent beds are purged with pure N_2 to desorb any amounts of iodine that may be physisorbed. The purge results for Test AG-1 are shown in Figure 4-2. This figure shows that only a small fraction of the iodine sorbed on Bed 1 was desorbed during the 31-hr purge period. At the start of the purge period, the Bed 1 outlet iodine level was over two orders of magnitude lower than the ~1.6 ppm range that occurred near the end of the sorption test. This concentration further decreased over another order of magnitude, to essentially the detection limit of the analysis method, after 5 hours of purging. The amount of iodine that was desorbed from Bed 1 started out within the first purge hour at about 0.003% of the iodine sorbed on Bed 1. After 31 purge hours, the cumulative amount of iodine desorbed from Bed 1 increased to about 0.05% of the sorbed iodine, but the increase in desorbed iodine has nearly flattened by that time.

The iodine that desorbed from Bed 1 during the purge period was sorbed in Beds 2 and 3, because shortly after purging was started, the iodine levels at the outlet of beds 2 and 3 had approached the detection limits. This is a likely trend that would occur in a full-scale process – as long as the full depth of a sorbent bed is not saturated, the remaining unsaturated sorbent can serve as a “getter” for physisorbed iodine that may slowly desorb from saturated sorbent pellets. The end result might possibly be efficient retention of the physisorbed iodine as it migrates from physisorption sites into sites were the iodine can chemisorb via reaction with the silver.

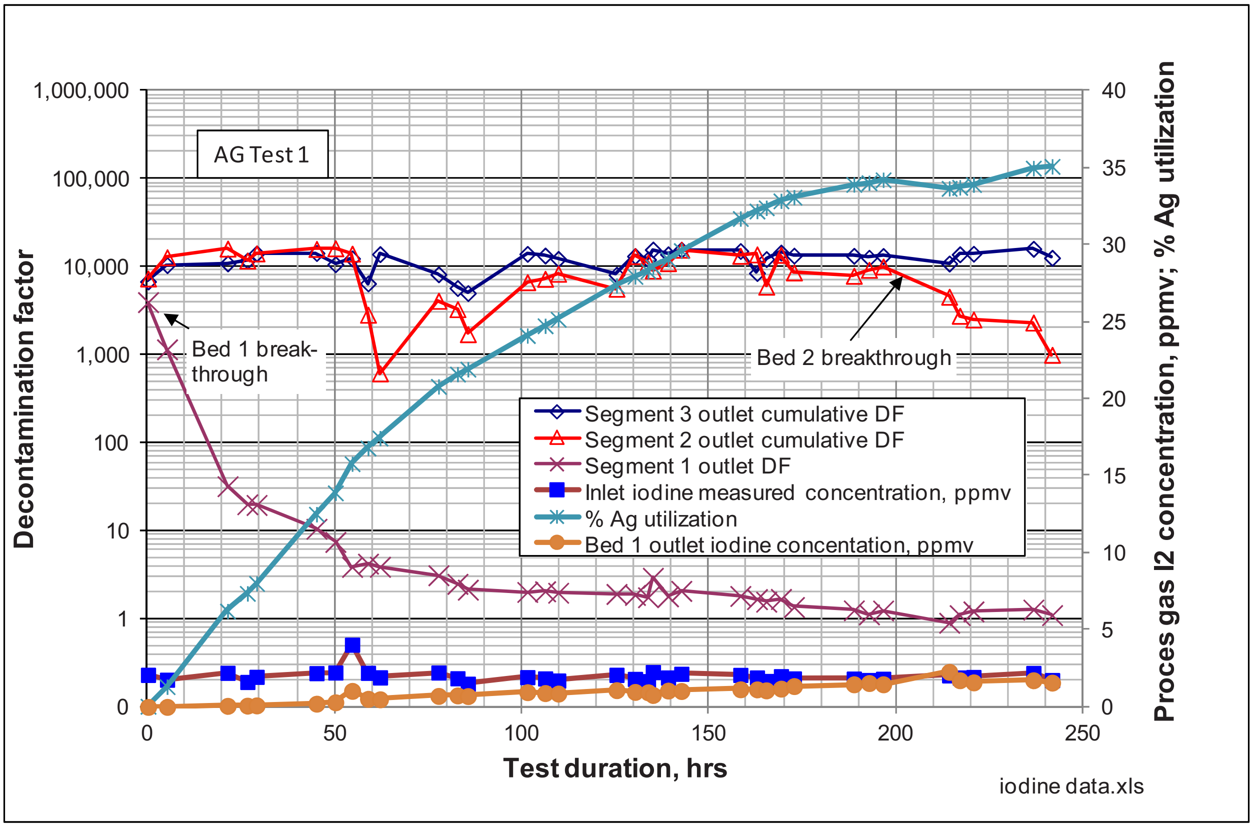


Figure 4-1. Test AG-1 iodine sorption results.

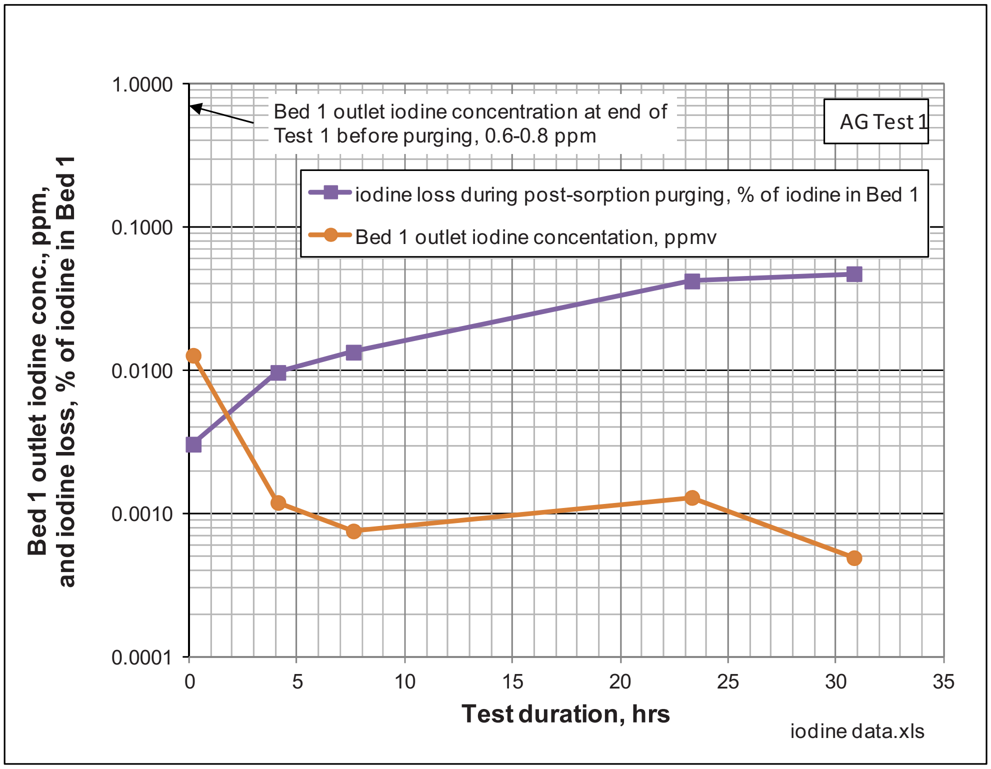


Figure 4-2. Test AG-1 purge results.

4.3 Test AG-2 Iodine Sorption Results

The iodine loading on the Bed 1 during Test AG-2 was calculated to be 17% based on the weight gain, and 22.3% based on the inlet and outlet gas measurements. The iodine loading on Bed 2 was 14% based on weight gain, and 19.7% based on inlet and outlet gas measurements.

Using the gas-phase iodine measurements, the maximum iodine decontamination factor (DF) was measured to be just over 10,000 in the 0.5-inch deep Bed 1, and on the order of 20,000 in Bed 3.

Process gas was sampled periodically during the duration of each test to enable determination of bed inlet and outlet iodine concentrations and sorption efficiencies as each test progresses. Figure 4-3 shows the trend in gaseous iodine concentrations, decontamination factors (DFs), and silver utilization on Bed 1 during the 242-hr Test AG-1. This figure shows that:

- The initial Bed 1 DF was over 10,000, essentially equal to that of the Bed 2. However, the DF for both Beds 1 and 2 rapidly decreased. This indicates that, under the test conditions, the mass transfer zone was at least 2 inches deep.
- Iodine DFs in Bed 3 generally ranged as high as 20,000 for most of the test, until breakthrough occurred at about hour 40. The long time it took for breakthrough of Bed 3 to occur indicates that the mass transfer zone was less than that the total bed 1 + 2 + 3 depth of 4 inches for these test conditions.
- According to the Bed 1 outlet iodine measurements, the Bed 1 appears to have gradually approached saturation during this test duration. The Bed 1 outlet iodine concentration was relatively flat and nearly the same as the inlet iodine concentration for about the last 24 hrs of the test.
- Bed 2 and 3 did not reach saturation during this test, even though Bed 2 appears to be approaching saturation.

After each test, the sorbent beds are purged with pure N_2 to desorb any amounts of iodine that may be physisorbed. The purge results for Test AG-2 are shown in Figure 4-4. At the start of the purge period, the Bed 1 outlet iodine level was over two orders of magnitude lower than the ~30 ppm range that occurred near the end of the sorption test. This concentration further decreased over another order of magnitude, to essentially the detection limit of the analysis method, after 15 hours of purging. The amount of iodine that was desorbed from Bed 1 started out within the first purge hour at under 0.002% of the iodine sorbed on Bed 1. After 24 purge hours, the cumulative amount of iodine desorbed from Bed 1 increased to about 0.01% of the sorbed iodine, but the increase in desorbed iodine has nearly flattened by that time.

The iodine that desorbed from Bed 1 during the purge period was sorbed in Beds 2 and 3, because shortly after purging was started, the iodine levels at the outlet of beds 2 and 3 had approached the detection limits. This is a likely trend that would occur in a full-scale process – as long as the full depth of a sorbent bed is not saturated, the remaining unsaturated sorbent can serve as a “getter” for physisorbed iodine that may slowly desorb from saturated sorbent pellets. The end result might possibly be efficient retention of the physisorbed iodine as it migrates from physisorption sites into sites were the iodine can chemisorb via reaction with the silver.

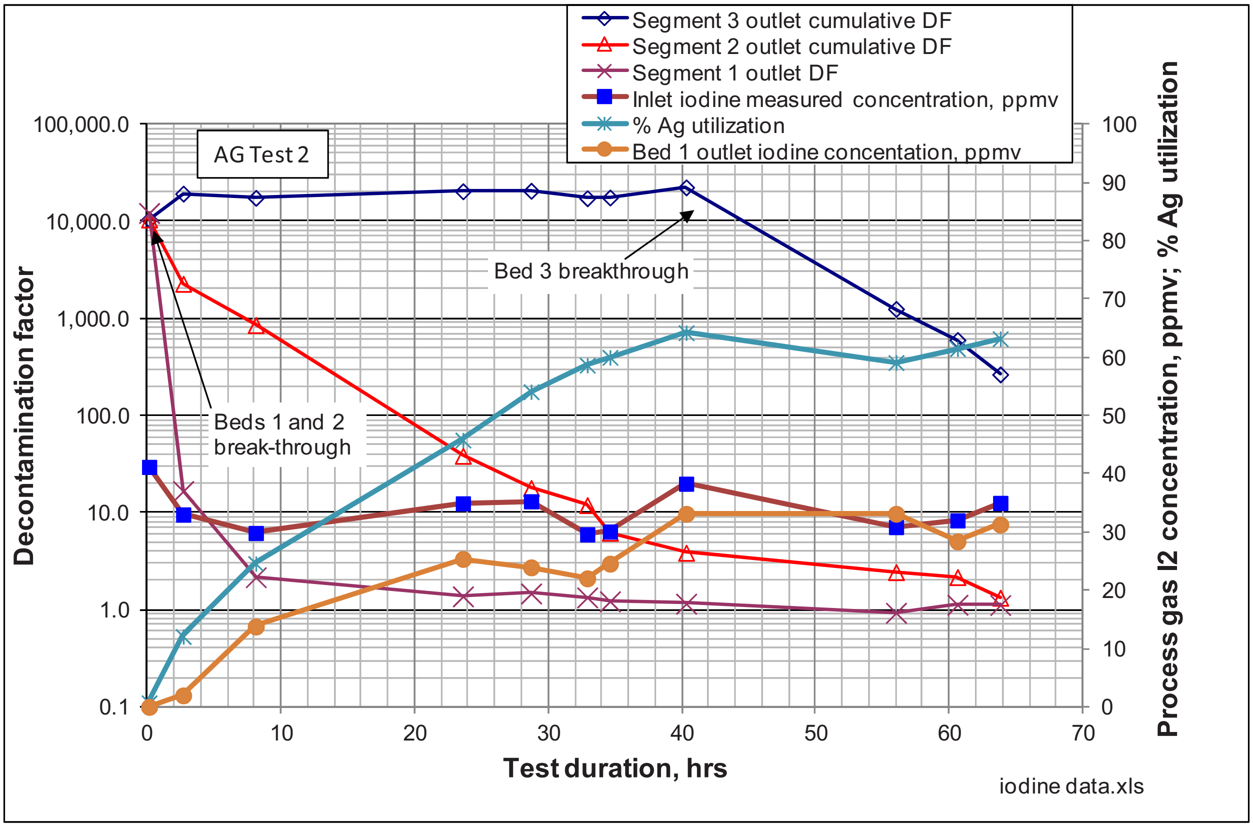


Figure 4-3. Test AG-2 iodine sorption results.

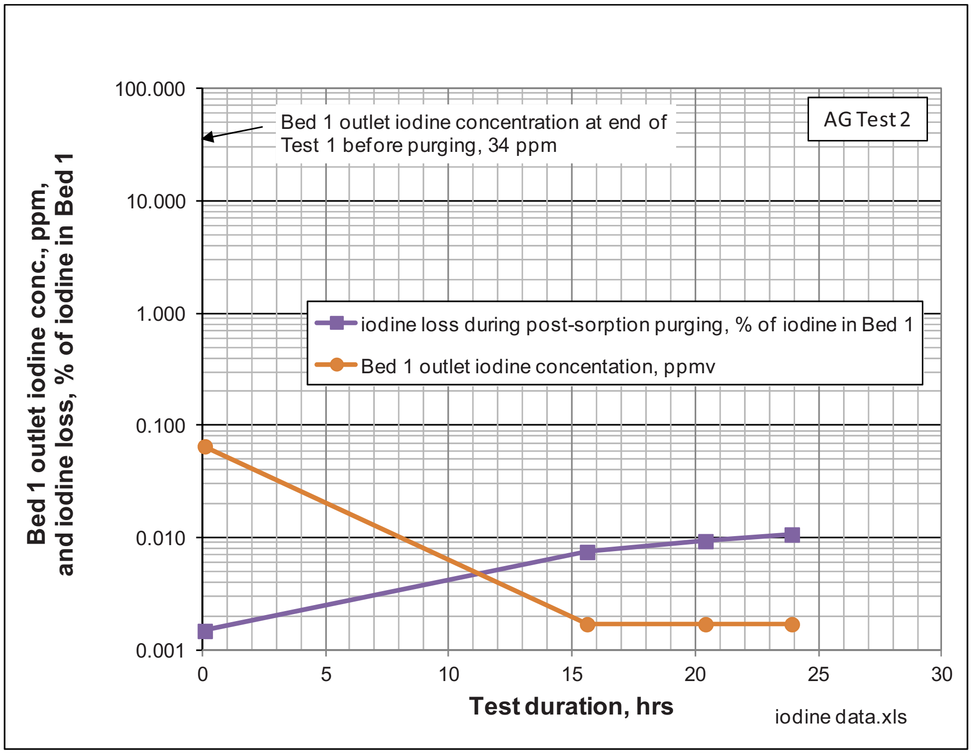


Figure 4-4. Test AG-2 purge results.

This page blank

5. CONCLUSIONS AND RECOMMENDATIONS

The Aerogel appears to have potential to be a very effective and efficient iodine sorbent. Under the test conditions, the iodine DFs reached at least 10,000 before breakthrough occurred. The mass transfer zone was between 0.5-2 inches under the conditions of Test AG-1, and between 2-4 inches under the conditions of Test AG-2. The capacity of the sorbent under the conditions of Test AG-1 was about 12 wt% (35% Ag utilization). The capacity of the sorbent under the conditions of Test AG-2 was about 22 wt% (63% Ag utilization).

This sorbent appears to achieve at least the range of DFs (~1,000 to 10,000) identified in previous studies (Jubin 2012) to be needed for used fuel reprocessing facilities in the U.S. to meet regulatory requirements for I-129 capture.

This page blank

6. REFERENCES

Haefner 2009 Haefner, D. R., and N. Soelberg, “Experimental Sorption Testing of Elemental Iodine on Silver Mordenite,” INL/EXT-09-16837, September 2009.

Haefner 2010 Haefner, D. R., and T. Watson, “Summary of FY 2010 Iodine Capture Studies at the INL,” INL/EXT-10-19657, August 2010.

INL 2011 “Gas Phase Iodine Capture Methods for Non-Radioactive Materials,” Laboratory Instruction 1287-070CFA, Revision 3, eCR No. 583874, February 16, 2011.

Jubin 2011 Jubin, Bob, et al, “Assessments and Options for Removal and Immobilization of Volatile Radionuclides from the Processing of Used Nuclear Fuel,” FCR&D-SWR-2011-000305, 31 August 2011.

Jubin 2012 Jubin, R.T, N.R. Soelberg, D.M. Strachan, and G. Ilas, “Position Paper on Practicable Performance Criteria for the Removal Efficiency of Volatile Radionuclides,” FCRD-SWF-2012-000091, INL-EXT-12-25410, March 30, 2012.

Pantano 2011 Pantano, Carlo, Tom Thomas, Jack Watson, and Chris Phillips, “FCR&D Off-Gas Sigma Team Peer Review, June 23-24, 2011.

Soelberg 2008 Soelberg, Nick, Mike Abbott, Daryl Haefner, and Bob Jubin, “Gaseous Fission Product Emissions Control During Spent Nuclear Fuel Recycling,” 235th ACS National Meeting and Exposition, New Orleans, LA, April 6-10, 2008.

Soelberg 2011 Soelberg, Nick and Veronica Rutledge, “Test Plan for Deep-Bed Iodine Sorption Studies: FY 12,” unpublished Idaho National Laboratory document, December 2011.