Design of, and Test Plan for, an Iodine and Tritium Capture System for an NO_2-Based Tritium Pretreatment Process

Nuclear Technology Research and Development

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

R. T. Jubin and B. B. Spencer

Oak Ridge National Laboratory
30 November 2018
ORNL/SPR-2018/1067

SUMMARY

The reprocessing of used nuclear fuel would release volatile radionuclides into the off-gas of a processing plant, including ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I. One potential simplification to the management of the off-gas streams could be achieved through an efficient tritium pretreatment (TPT) step in which the UO_2 fuel is oxidized either by air or by NO_2 before dissolution. Oxidation of the UO_2 fuel matrix results in the release of tritium contained within. Upfront removal of tritium from the fuel in a pretreatment step, followed by the abatement of tritium, can minimize or eliminate the distribution of tritium throughout the plant, also decreasing or eliminating the need for tritium capture on multiple off-gas streams. The use of NO_2 as the oxidant in an advanced tritium pretreatment (ATPT) allow the oxidation to be performed at lower temperatures and may result in the quantitative release of iodine from the fuel.

The ATPT off-gas will contain up to 75 vol% NO_2 gas. Spencer et al. (2017) identified the most promising iodine sorbent as silver nitrate–impregnated alumina (AgA) and the most promising tritium sorbents as 3A molecular sieve (3A MS) and silica gel for radionuclide capture from ATPT off-gas streams. An initial series of tests were conducted in fiscal years 2017–2018 (Jubin et al. 2018) with the intent of demonstrating the recovery of iodine and tritium using these sorbents from a recirculating gas stream that simulated the NO_2 recycle loop envisioned for the ATPT system. These initial tests showed low tritium recoveries and significant variations in the iodine recovery on the AgA. Ultimately it was concluded, following disassembly of the system, that corrosion within the system was at least partially the cause of the poor recovery for both species of interest. All components of that system were disposed of at the end of the analysis.

One of the conclusions drawn from those tests pointed to the reconsideration of the materials of construction. Based on that recommendation a new system has been designed that will use high nickel alloys wherever possible, a redesigned surge tank, feed system and a more modular system design that will support testing of the system with incremental increases in complexity to allow the isolation of any element that results in changes to recovery of target species. A multifaceted test plan has been developed for the test system that includes a total of 15 tests and a total of 27 individual runs.

This page is intentionally left blank.

CONTENTS

FIGURES

TABLES

This page is intentionally left blank.

ACRONYMS

3A MS	3 angstrom molecular sieve
AgA	$AgNO_3$-impregnated alumina
ATPTOG	advanced tritium pretreatment off-gas
DOG	dissolver off-gas
EG	ethylene glycol
FY	fiscal year
IC	iodine capture [phase]
IP	iodine purge
LPM	liters per minute
NAA	neutron activation analysis
ORNL	Oak Ridge National Laboratory
TC	tritium capture [phase]
TPTOG	tritium pretreatment off-gas
TPT	tritium pretreatment
TR	tritium sorbent regeneration [phase]

This page is intentionally left blank.

DESIGN OF, AND TEST PLAN FOR, AN IODINE AND TRITIUM CAPTURE SYSTEM FOR AN NO_2-BASED TRITIUM PRETREATMENT PROCESS

1. INTRODUCTION

The reprocessing of used nuclear fuel will release four volatile radionuclides into the off-gas of a processing plant. These radionuclides are ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I. For a reprocessing plant sited within the United States and governed by US regulations, the abatement of some or all these radionuclides from the plant off-gas will be required before discharge of that gas to the environment. In some cases, the level of abatement required is significant (Jubin et al. 2012).

Traditional aqueous reprocessing dissolves sheared used fuel in hot nitric acid solution. As the fuel dissolves, the volatile radionuclides contained within the fuel are evolved into the dissolver off-gas stream. There is also some fraction of the volatile radionuclides that remain in the dissolver solution, and those radionuclides are transferred to subsequent processing steps and to the process off-gas streams generated by those processes. The distribution of the radionuclides into multiple liquid and gaseous streams results in the need to manage volatile radionuclides emissions from multiple off-gas streams associated with the reprocessing plant.

A potential simplification of the off-gas management system can be achieved through an efficient tritium pretreatment (TPT) step in which the UO_2 in the used fuel is oxidized prior to dissolution. Oxidation of the UO_2 fuel matrix results in the release of tritium contained within the fuel matrix. Traditional TPT is conducted by oxidizing the fuel with a dry O_2-bearing gas stream at high temperatures. Upfront removal of tritium from the fuel in a pretreatment step, followed by the abatement of tritium from the TPT off-gas stream, can minimize or eliminate the distribution of tritium throughout the plant, also decreasing or eliminating the need for tritium capture on multiple off-gas streams.

An advanced variant of the O_2-based TPT process uses NO_2, a stronger oxidant, as the gaseous reagent. The use of NO_2 allows TPT to be performed at lower temperatures and may result in the quantitative release of iodine from the fuel. Upfront removal and abatement of iodine and tritium could result in substantially further simplification of the off-gas treatment processes. The advanced tritium pretreatment off-gas (ATPTOG) will contain up to 75 vol% NO_2 gas. Very little data is available on the performance of traditional iodine sorbents, such as silver-exchanged zeolites, and traditional tritium adsorbents, such as molecular sieves, under the conditions present in the ATPTOG system.

A previous report (Spencer et al. 2017) identified the most promising iodine sorbent as silver nitrate–impregnated alumina (AgA) and the most promising tritium sorbents as 3Å molecular sieve (3A MS) and silica gel for radionuclide capture from ATPTOG streams. The reaction between silver nitrate ($AgNO_3$) and I_2 to form AgI is thermodynamically favorable, and minerals impregnated with $AgNO_3$ have been used for I_2 removal from the dissolver off-gas streams at the La Hague fuel reprocessing plant in France. However, the dissolver off-gas stream contains only ~2 vol% NO_x gaseous species, far below the levels expected in the ATPTOG stream. The preliminary testing of AgA, 3A MS, and silica gel for iodine and tritium removal from ATPTOG streams is documented in *Assembly and Testing of a Tritium and Iodine Removal System for Use with Advanced Tritium Pretreatment*, NTRD-MRWFD-2017-000157 (Jubin et al. 2017).

Tests were conducted in fiscal year (FY) 2017 and early FY 2018 (Jubin et al. 2018) with the intent to demonstrate the recovery of iodine and tritium using these sorbents from a recirculating gas stream that simulated the NO_2 recycle loop envisioned for the ATPT system. These initial tests showed low tritium recoveries and significant variations in the iodine recovery on the AgA. These results were unexpected, and a number of additional exploratory tests were performed in an attempt to account for the low recoveries. These tests failed to fully explain the low recovery performance and ultimately prompted a full system disassembly to assess whether there was holdup of tritium and iodine within the system. The surge tank, which had been reused from a previous experimental system, showed signs of corrosion, and smears taken at various locations were positive for tritium at multiple locations. Several corroded fittings were removed from the surge tank, and both iodine and tritium were found in the corrosion products. No corrosion was observed at other visually inspected locations, and no other inspected locations smeared positive for tritium.

One of the conclusions drawn from those tests pointed to the reconsideration of the materials of construction. Although the surge tank used in the initial tests was constructed of stainless steel, which is considered to be compatible with NO_2 gas and N_2O_4 liquid, other more corrosion-resistant materials should be carefully considered. Iodine is known to corrode stainless steel in the presence of water. It was also noted that a second possibility is that NO_2 itself contributed to the corrosion of the system. The surge tank, which was the only visibly corroded component, was not heated during testing.

The overarching goals of the tests described in this plan are two-fold. The first goal is to demonstrate the ability recovery both the iodine and tritium that would be released during TPT in a manner that the releases from the fuel can be quantified. The second goal is to demonstrate the combined recovery system that could operate on any of the three proposed TPT modes (once-through air or O_2, recirculating air or O_2, or recirculating NO_z). These tests will be, in many ways, similar in nature to the previous series of tests, particularly those tests used to explore the origin of the limited tritium and iodine recovery.

2. MATERIALS AND METHODS

2.1 Test Loop

The experimental methodology for the tests was reported previously in Jubin et al. (2017), and the initial tests were reported in Jubin et al. (2018). The design of the test loop is very similar to the one used in the initial series of tests with a few additional features. The experimental setup is shown in Figure 1. The primary loop of this system will be constructed using a high nickel alloy. The system will be modular in design such that the tests will be conducted as components are added. This will result in a sequence of increasing system complexity with the intent of ensuring that any changes in the amount of either tritium or iodine that is recovered is due to specific changes in operating modes and not due to losses within the system. Unlike the previous test loop, this loop is designed to operate in three possible TPT modes (once-through air or O_2, recirculating air or O_2, or recirculating NO_2). A major change is in the design of the 1 L surge tank, which will now have provisions for heating to ensure that the NO_2 will not condense there, and the return line will extend to near the bottom of the tank to minimize dead space within the tank.

Tritiated water (or deuterated water as a non-radioactive surrogate) and / or, iodine will be introduced in the system as required for a specific test through a modified loading system. This modified system is shown in Figure 2. This feed system will be installed in the line between the recirculating pump and the three-way valve prior to the iodine and tritium trapping systems. This feed system includes a valved gas bypass line and two sections each containing a charging port. The charging sections have block valves at each end and a removable cap on a tee in the middle of the charging section. Before a test, with the bypass valves open and the block valves for the charging sections closed, the caps are removed and a known amount of material is introduced into the load chambers and the caps are replaced. As with the rest of the system lines, the charging chambers are heat traced but they are on a separate control that allows them to be heated independently. At the desired time the block valves on the individual charging sections are opened and the associated bypass valve is closed allowing the gas stream to pass through the charging section. The design allows direct flow of the full stream through either of both of the charging sections.

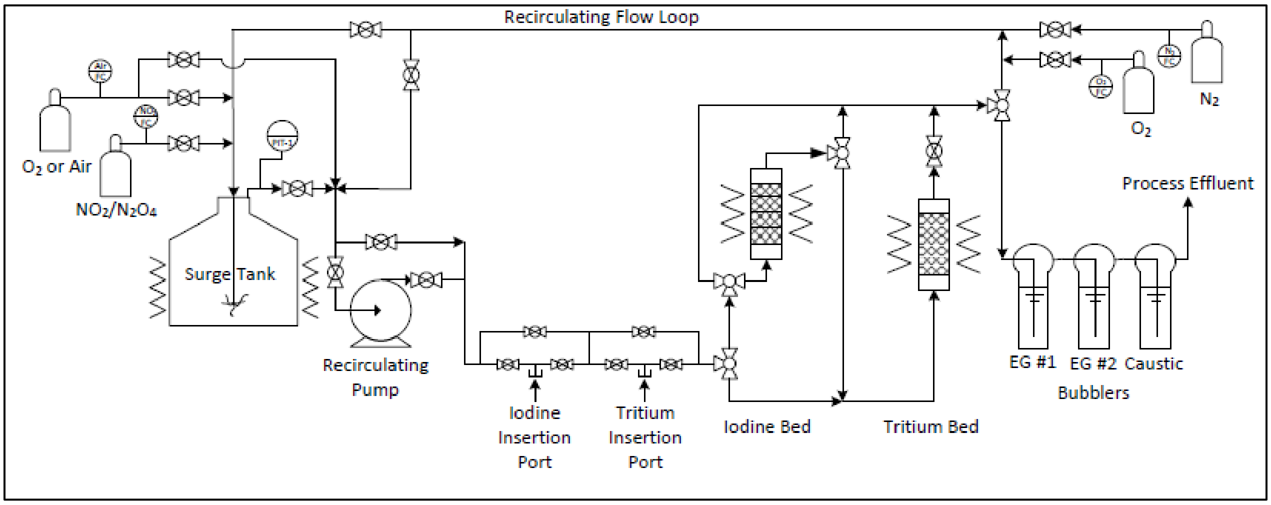

Figure 1: Schematic of iodine and tritium sorbent test system.

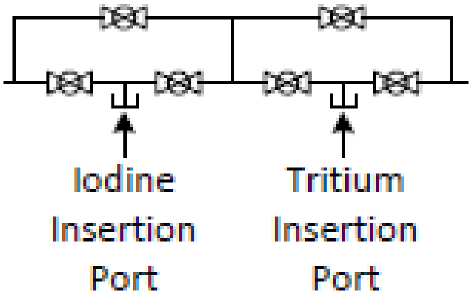

Figure 2: Sample charging system design.

2.2 Materials

2.2.1 Tritium Sorbents

Both 3A MS and silica gel will be tested as potential tritium sorbents. The tritium column will be loaded to a depth of 10 cm. These will be loaded at an operating temperature of 40 °C. Silica gel and 3A MS are intended for use as regenerative sorbents, in which the adsorbed tritium (as tritiated water or tritiated nitric acid) is loaded onto the sorbent at operating temperature and then subsequently desorbed at high temperature into a small-volume gas stream for recovery and conversion to a waste form. The manufacturer-recommended desorption temperatures for 3A MS and silica gel are >250 °C and >90 °C, respectively.

2.2.2 Iodine Sorbent

Before the start of each test, the iodine column will be loaded with AgA. This material will be prepared in the same manner as described in Jubin et al. (2018). The column will be separated into discrete segments with layers of quartz wool between the segments. The length of the iodine sorbent bed is 10 cm.

2.2.3 Tritium Feed

Each test will use 100 µL of either deuterated or tritiated water. This amount of water is greater than the amount expected of HTO in actual used nuclear fuel with a burnup of 60 GWd/MTIHM or 1 µL, but it is reflective of the potential need to add 100 fold additional water to achieve a tritium decontamination factor of 100 at these very low concentrations. Deuterated or tritiated water will be introduced in the system through the modified charging system. The tritium / deuterium charging section is an isolated section of line with a removable fitting to allow for the introduction of the sample. Prior to the start of the test the valves are configured to bypass both charging sections. The cap on the second charging section downstream of the pump is opened and a known amount material is introduced into the load chamber, and the cap is replaced. At the desired time in a specific run, the two block valves at the ends of this charging section are opened and the bypass valve for that section is closed. With the load chamber heated, it is expected that both the crystalline iodine and water would transfer into the gas recirculation loop quickly and completely.

2.2.4 Iodine Feed

Iodine will be introduced as crystalline I_2. Approximately 0.13 g will be used in each test. This amount of iodine is based on the expected quantity of total iodine in 0.33 kg of used nuclear fuel with a burnup of 60 GWd/MTIHM. A similar charging system to that for the tritium is used. This is the charging section nearest the recirculation pump.

3. TEST DESCRIPTIONS

The overarching goals of these tests are two-fold. The first goal is to demonstrate the ability to recover both the iodine and tritium that would be released during TPT in a manner that the releases from the fuel can be quantified. The second goal is to demonstrate the combined recovery system that could operate on any of the three proposed TPT modes (once-through air or O_2, recirculating air or O_2, or recirculating NO_2). The tests described below will be, in many ways, similar in nature to the previous series of tests, particularly those tests used to explore the origin of the limited tritium and iodine recovery.

A total of 15 categories of tests with a total of 27 individual runs are planned. The details of each test category and the number of planned replicates are summarized in Table 1. Tests 1–5 are all performed with deuterated water as a cold stand-in for tritiated water, tests 6–10 are iodine only, and tests 11–15 used both iodine and deuterated or tritiated water. Approximately half of the individual runs will use 40%–50% NO_2 as a carrier gas. The recommended sequence is to complete one pass of tests 1–10 with replicates of tests 5 and 10 prior to completing the balance of the replicates of these tests. Based on the results of the first series of tests, some replicates may not be required.

These tests are based on the assumption that the selected sorbent will perform as expected in this environment and that the limited recovery in the initial tests was the result of the corrosion noted within the system and not the fault of the sorbent. Should recovery issues arise, the modular design will allow for the replacement of the iodine and or tritium capture beds with an alternate system.

During most of the individual tests, there are four distinct phases:

1. Iodine capture (or simulated iodine capture) (IC)
2. Tritium capture (TC)
3. Tritium sorbent regeneration (TR)
4. Iodine purge (IP)

Between each of the phases the valve lineup will be changed to provide the appropriate flow paths for the gas stream. Several of the tests (e.g., once-through) will eliminate one or more of the phases. The individual test descriptions and the associated flow path drawing will focus mainly on the IC and TC phases. A brief description of the other phases are presented below. In these descriptions and associated figures, the heavy black lines are the common flow paths. Depending on the test system configuration, portions of the system may be bypassed and alternate pathways used. These alternate pathways are represented by the red and blue lines in Figures 3 and 4..

3.1 Iodine Capture Phase

This phase typically involves the initial loading of the iodine trap. This phase is simulated or bypassed in tests 1–5.

3.2 Tritium Capture Phase

After (IC) and recirculation, the heat tapes and recirculation pump were turned off, and the tritium bed is heated to 40 °C. The flow path was altered so that the gas stream does not pass through the iodine bed but passes through the tritium bed and then passes out of the system through bubblers of ethylene glycol (EG) , sodium hydroxide (NaOH), or both, as shown in Figure 3.

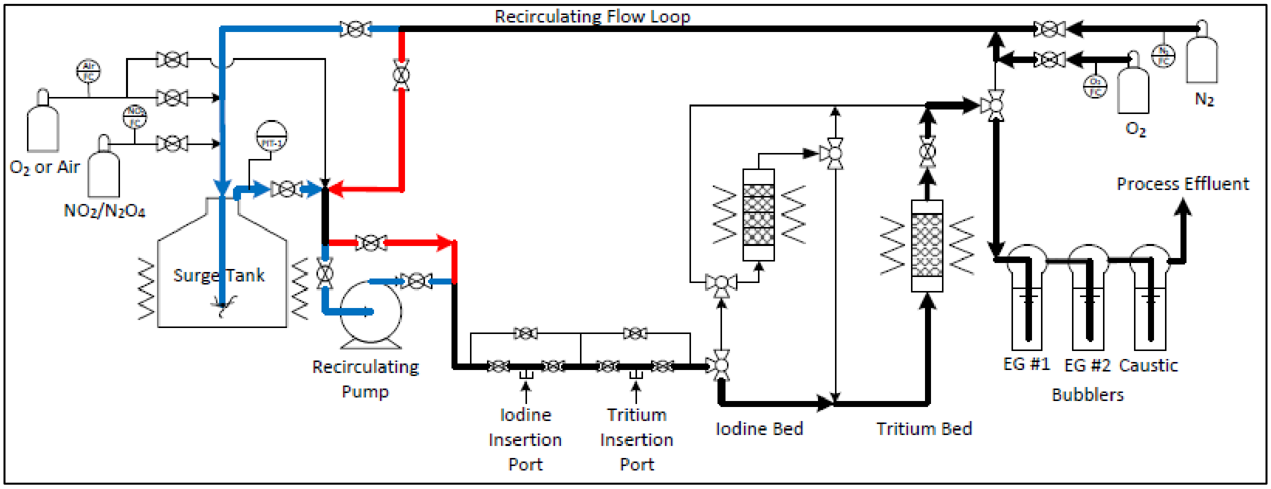

Figure 3: Gas flow path (bolded) during tritium regeneration phase.

3.3 Tritium Sorbent Regeneration Phase

The system is again sealed off, and the temperature of the tritium bed is raised to the selected regeneration temperature. After reaching the setpoint, the system is opened, and the bed is purged with oxygen at 0.5 L/min for 2 hours. The effluent from the tritium column flows through two ethylene glycol scrubbers and one NaOH scrubber, with the scrubber solutions sampled between the TC and TR phases of testing. The flow path for the oxygen purge is shown in Figure 3.

3.4 Iodine Sorbent Purge

Upon completion of tritium regeneration, the system valving alignment is modified so that the tritium column is sealed from the rest of the system, and the iodine column is included in the flow path (Figure 4). The iodine column is held at 150 °C and purged with oxygen at 0.5 L/min for 2 hours. The effluent passes through one ethylene glycol and one NaOH scrubber. The scrubber solutions are sampled between the TR and IP phases of testing.

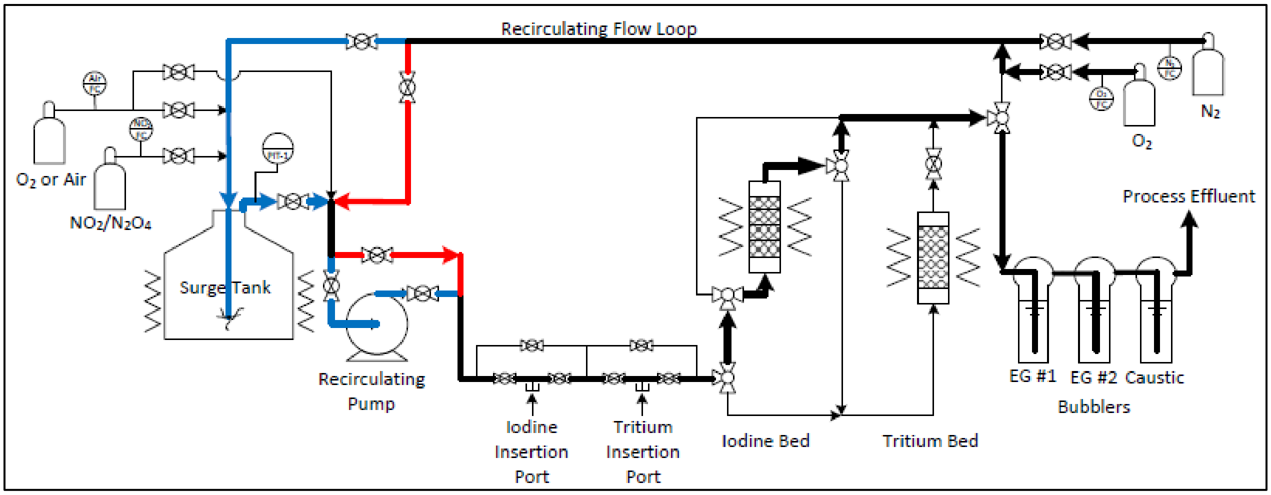

Figure 4: Gas flow path (bolded) during iodine sorbent purge phase.

3.5 Descriptions of the Individual Tests

3.5.1 Test 1: Once-through Deuterium Recovery

The objective of this test is to demonstrate the “quantitative” or baseline recovery of the injected deuterium in the ethylene glycol (EG) traps. The flowsheet for this test is shown in Figure 5. Deuterated water will be introduced in the system through one of the charging ports described above. Both the tritium trap and the iodine trap sections will be in place but will not contain sorbent. An air carrier gas is introduced at a rate of 0.25 L/min and passed through the system, bypassing the recirculation pump, through the charging section and empty tritium bed before passing through the glycol traps.

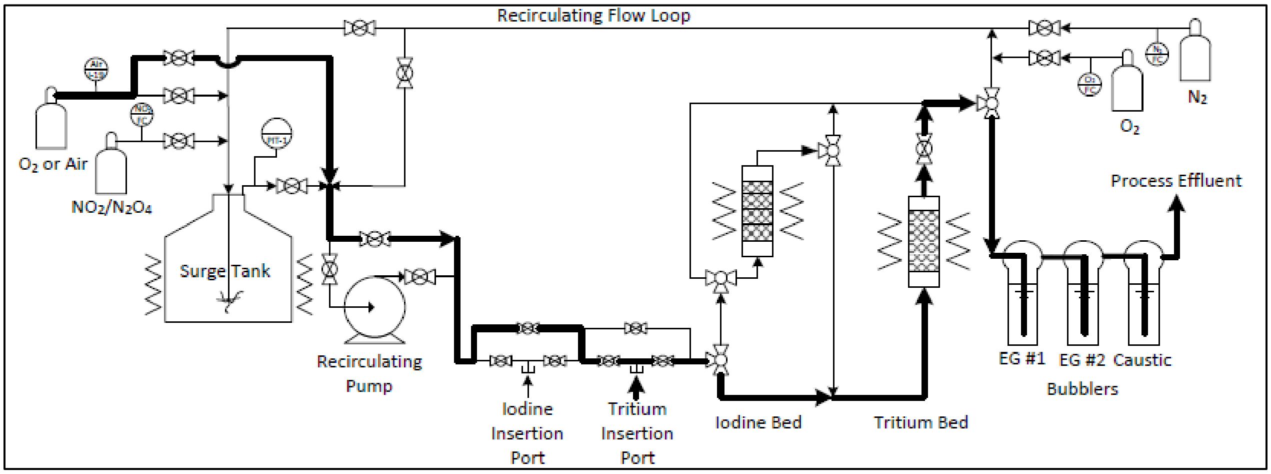

Figure 5: Schematic of iodine and tritium sorbent test system as configured for tests 1 and 2.

Table 1: Test descriptions.

Test ID	**Sorbent (Iodine / Tritium)**	**Mode of Operation**	**Carrier Gas**	**Sorbates**	**Tritium Desorption**	**No. of Runs**	**Notes**
ATPT19–1	None / None	Once-through	Air	Deuterated Water	N/A	3	Establish deuterium recovery in ethylene glycol baseline
ATPT19–2	None / Silica gel	Once-through	Air	Deuterated Water	90 °C	3	Establish deuterium desorption recovery in ethylene glycol baseline
ATPT19–3	None / Silica gel	Recirculation	Air	Deuterated Water	90 °C	1	Establish deuterium desorption recovery in ethylene glycol baseline
ATPT19–4a	None / Silica gel	Recirculation / w Surge tank	Air	Deuterated Water	90 °C	2	Establish deuterium desorption recovery in ethylene glycol baseline Compare deuterium purge / capture methods
ATPT19–4b	None / Silica gel	Recirculation / w Surge tank	Air	Deuterated Water	90 °C	2	Establish deuterium desorption recovery in ethylene glycol baseline Compare deuterium purge / capture methods
ATPT19–5	None / Silica gel	Recirculation / w Surge tank	NO_2	Deuterated Water	90 °C	2	Establish deuterium desorption recovery in ethylene glycol baseline
ATPT19–6	None / None	Once-through	Air	Iodine	N/A	3	Establish iodine recovery in ethylene glycol and caustic baseline
ATPT19–7	AgA / None	Once-through	Air	Iodine	N/A	2	Establish iodine recovery on AgA in ethylene glycol and caustic baseline
ATPT19–8	AgA / None	Recirculation	Air	Iodine	N/A	1	Establish iodine recovery on AgA
ATPT19–9	AgA / None	Recirculation / w Surge tank	Air	Iodine	N/A	2	Establish iodine recovery on AgA
ATPT19–10	AgA / None	Recirculation / w Surge tank	NO_2	Iodine	N/A	3	Establish iodine recovery on AgA
ATPT19–11	AgA / Silica Gel	Once-through / w Surge tank	Air	Iodine/ Deuterated Water	90 °C	1	Establish iodine recovery on AgA deuterium desorption recovery in ethylene glycol baseline
ATPT19–12	AgA / Silica Gel	Recirculation / w Surge tank	Air	Iodine/ Deuterated Water	90 °C	2	Establish iodine recovery on AgA deuterium desorption recovery in ethylene glycol baseline
ATPT19–13	AgA / Silica Gel	Recirculation / w Surge tank	Air	Iodine/ Tritiated Water	90 °C	3	Establish iodine recovery on AgA deuterium desorption recovery in ethylene glycol baseline
ATPT19–14	AgA / Silica Gel	Recirculation / w Surge tank	NO_2	Iodine/ Deuterated Water	90 °C	2	Establish iodine recovery on AgA tritium desorption recovery in ethylene glycol baseline
ATPT19–15a	AgA / Silica Gel	Recirculation / w Surge tank	NO_2	Iodine/ Tritiated Water	90 °C	3	Establish iodine recovery on AgA tritium desorption recovery in ethylene glycol baseline
ATPT19–15b	AgA / 3A MS	Recirculation / w Surge tank	NO_2	Iodine/ Tritiated Water	250 °C	3	Establish iodine recovery on AgA tritium desorption recovery in ethylene glycol baseline

3.5.2 Test 2: Once-through Deuterium Sorption/Desorption and Recovery

The objective of this test is to demonstrate the "quantitative" recovery of the injected deuterium that is sorbed on the silica gel and in the ethylene glycol traps. The flowsheet for this test is shown in Figure 5. Deuterated water will be introduced in the system through one of the charging ports as was used in the previous tests. The iodine trap section will be in place but will not contain sorbent. An air carrier gas is introduced at a rate of 0.25 L/min and passed through the system, bypassing the recirculation pump, through the charging section and tritium bed before passing through the glycol traps. The system will operate in the loading mode for 30 min with the silica gel trap at 40 °C. At the end of the 30 min loading period, the glycol traps will be sampled to determine the amount of deuterium that penetrated the bed. The regeneration of the "tritium" trap will be heated to 90 °C using the same methods as used in the initial tests reported by Jubin et al. (2018).

In the regeneration portions of those tests, the system was then sealed off, and the temperature of the tritium bed was raised to the selected regeneration temperature (90 °C for silica gel and 250 °C for the 3A MS). After reaching the setpoint, the system is opened, and the bed is purged with oxygen at 0.5 L/min for 2 hours. The effluent from the tritium column passes through two ethylene glycol scrubbers and one NaOH scrubber, with the scrubber solutions sampled between the collection and regeneration phases of testing.

3.5.3 Test 3: Recirculation Deuterium Sorption/Desorption and Recovery

The objective of this test is to demonstrate the "quantitative" recovery of the injected deuterium that is sorbed on the silica gel and in the ethylene glycol traps. The flowsheet for this test is shown in Figure 6. Deuterated water will be introduced in the system through the charging port. The tritium trap will be charged with silica gel. Initially the "tritium" trap will be valved out to simulate an "iodine" capture mode. The iodine trap section will be in place but will not contain sorbent. An air carrier gas is to be recirculated at a rate of ~0.25 L/min either through the empty iodine bed or through the bypass line. The system will be operated in the "iodine" capture mode for 30 min. At the end of the 30 min loading period, the iodine trap will be valved out.

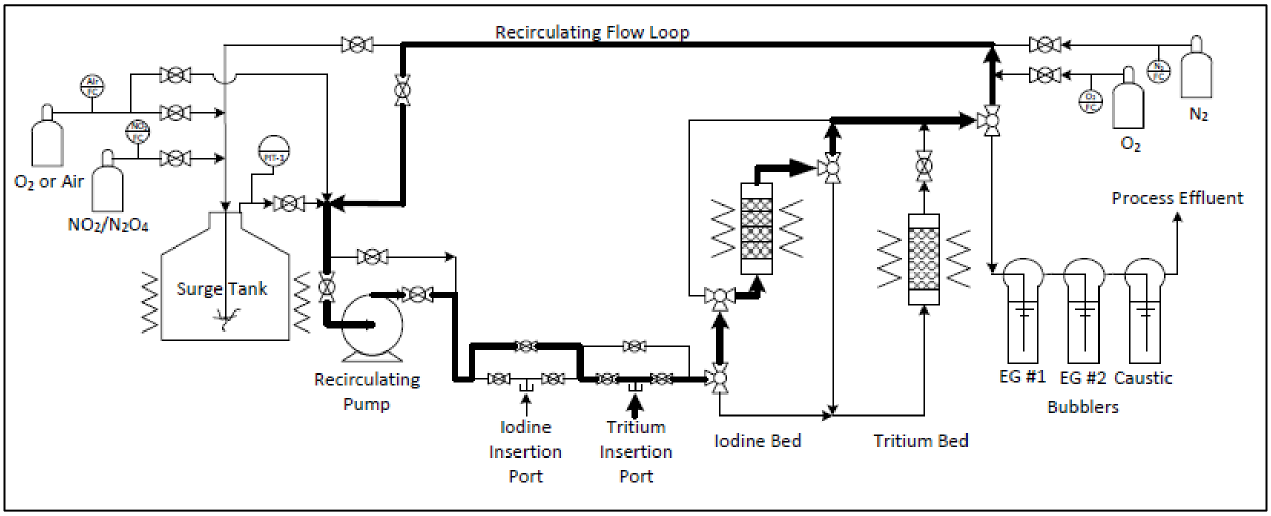

Figure 6: Schematic of iodine and tritium sorbent test system as configured for test 3.

After simulated IC and recirculation, the heat tapes and recirculation pump are to be turned off and the tritium bed heated to 40 °C. The flow path is altered so that the gas stream does not pass through the iodine bed but would pass through the tritium bed and then pass out of the system through bubblers of ethylene glycol, sodium hydroxide (NaOH), or both. To ensure that the deuterium-bearing gas stream is fully discharged through the scrubbers, oxygen is introduced at a rate of 0.25 L/min. The glycol and caustic traps will be sampled and replaced as needed. The glycol will be analyzed to determine the amount of deuterium that penetrated the tritium bed. The regeneration of the "tritium" trap will be the same as used in test 2.

3.5.4 Test 4: Recirculation and Surge Tank Operation with Deuterium Sorption/Desorption and Recovery

The objective of this test is to demonstrate the "quantitative" recovery of the injected deuterium that is sorbed on the silica gel and in the ethylene glycol traps with recirculation and surge tank. The flowsheet for this test is shown in Figure 7. Deuterated water will be introduced in the system through the charging port. The tritium trap will be charged with silica gel. Initially the "tritium" trap will be valved out. The iodine trap section will be in place but will not contain sorbent. An air carrier gas is to be recirculated at a rate of ~0.25 L/min either through the empty iodine bed or through the bypass line. The system will be operated in the "iodine" capture mode for 30 min. At the end of the 30 min loading period, the iodine trap will be valved out.

After IC and recirculation, the heat tapes and recirculation pump are to be turned off and the tritium bed heated to 40 °C. The flow path is altered so that the gas stream does not pass through the iodine bed but would pass through the tritium bed and then pass out of the system through bubblers of ethylene glycol, sodium hydroxide (NaOH), or both. To ensure that the deuterium-bearing gas stream is fully discharged through the scrubbers, oxygen is introduced at a rate of 0.25 L/min. The glycol and caustic traps will be sampled and replaced. The glycol will be analyzed to determine the amount of deuterium that penetrated the tritium bed. The regeneration of the "tritium" trap will be the same as used in test 2.

This test will be repeated a second time with an alternate "tritium" capture mode of operation. This mode involves repeated pressurization/depressurization of the system as was done in the FY 2017–2018 test series. It is believed that the redesigned surge tank should eliminate the need for this alternate process. This test is to confirm the two methods achieve the same results. After the simulated IC phase and recirculation, the heat tapes and recirculation pump are turned off and the tritium bed heated to 40 °C. The flow path is altered so that the gas stream does not pass through the iodine bed but passes through the tritium bed and then passes out of the system through bubblers of ethylene glycol, sodium hydroxide (NaOH), or both. To ensure that the deuterium-bearing gas stream is fully discharged through the scrubbers, oxygen is added to the system to until a pressure of 3.0 atm is reached and then the gas is bled down through the tritium bed and bubblers to ~1.1 atm. The system is pressurized and depressurized five times. These pressurization/depressurization cycles should result in >99% of the gas-phase deuterium being discharged through the tritium bed and into the ethylene glycol and NaOH scrubbers. Any tritium adsorbed by the solid sorbents would remain in the system.

3.5.5 Test 5: Recirculation and Surge Tank Operation with Deuterium Sorption/Desorption and Recovery

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed deuterium and in the ethylene glycol traps with recirculation and surge tank at ATP NO_2 levels. In essence, this is the same as test 4 using ~45% NO_2 instead of air as the carrier gas. The flowsheet for this test is shown in Figure 7.

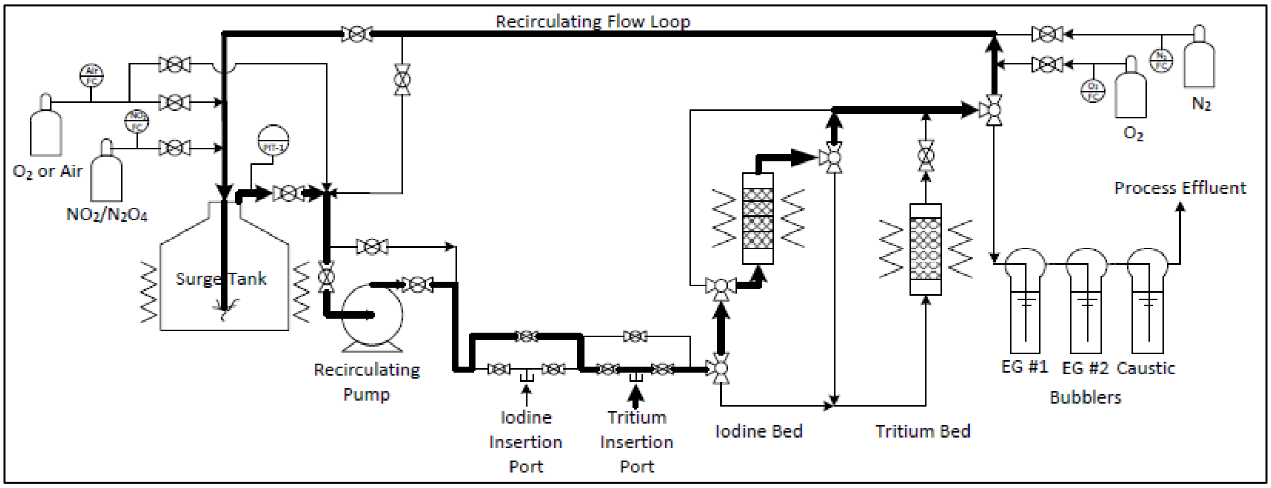

Figure 7: Schematic of iodine and tritium sorbent test system as configured for tests 4 and 5.

The recirculation system is closed off to the environment, and the system is evacuated to an absolute pressure of 0.30 atm. This vacuum level is to be held for ~30 min to verify that the system is leak tight. After determination of the system integrity (observably leak tight for the experimental durations), NO_2 is delivered to the system from a tank of liquid N_2O_4 until the system pressure is raised to ~0.83 atm and oxygen is added until the final pressure of the system is ~1.14 atm. This results in a total system NO_2 partial pressure of 0.53 atm and an NO_2 concentration of 47% in the gas phase.

Deuterated water will be introduced in the system through an isolation lock. The tritium trap will be charged with silica gel. Initially the “tritium” trap will be valved out. The iodine trap section will be in place but will not contain sorbent. The carrier gas is to be recirculated at a rate of ~0.25 L/min either through the empty iodine bed or through the bypass line. At the end of the 30 min simulated “iodine” capture or loading period, the iodine trap will be valved out.

After simulated IC and recirculation, the heat tapes and recirculation pump are to be turned off and the tritium bed heated to 40 °C. The flow path is altered so that the gas stream does not pass through the iodine bed but would pass through the tritium bed and then pass out of the system through bubblers of ethylene glycol and/or sodium hydroxide (NaOH). To ensure that the deuterium-bearing gas stream is fully discharged through the scrubbers, oxygen is introduced at a rate of 0.25 L/min. (NOTE: This assumes that the two methods of “tritium” capture results in equal recovery. If not, the best method will be used.) Sample the glycol and caustic traps. Replace the traps as needed. The glycol will be analyzed to determine the amount of deuterium that penetrated the tritium bed. The regeneration of the “tritium” trap will be the same as used in test 4.

3.5.6 Test 6: Once-through Iodine Recovery

The objective of this test is to demonstrate the “quantitative” recovery of the injected iodine in the ethylene glycol and caustic traps. The flowsheet for this test is shown in Figure 8. Iodine will be introduced in the system through a charging port. Both the tritium trap and the iodine trap sections will be in place but will not contain sorbent. An air carrier gas is introduced at a rate of 0.25 L/min and passed through the system, bypassing the recirculation pump, through the charging section and empty iodine bed prior to passing through the glycol and caustic traps.

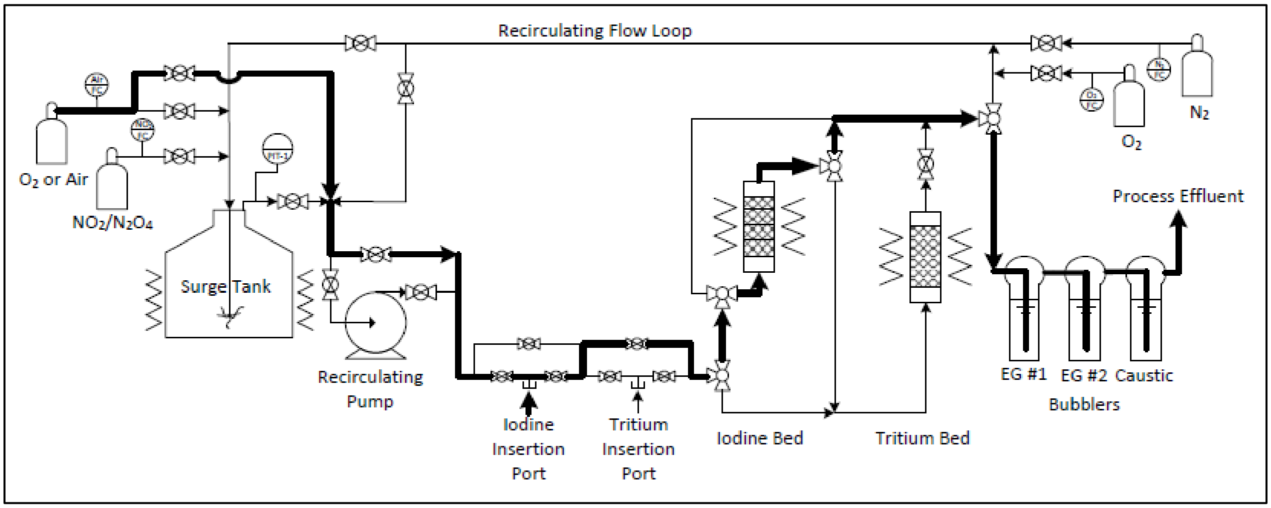

Figure 8: Schematic of iodine and tritium sorbent test system as configured for tests 6 and 7.

3.5.7 **Test 7: Once-through Iodine Sorption/Desorption and Recovery**

The objective of this test is to demonstrate the “quantitative” recovery of the injected and sorbed iodine on the AgA sorbent media. The flowsheet for this test is shown in Figure 8. Iodine will be introduced in the system through a charging port as was used in the previous tests. The iodine trap will be charged with AgA and operated at 150 °C. The tritium trap section will be in place but will not contain sorbent. An air carrier gas is introduced at a rate of 0.25 L/min and passed through the system, bypassing the recirculation pump, through the charging section and iodine bed prior to passing through the glycol and caustic traps. The system will operate in the loading mode for 30 min. At the end of the 30 min loading period, the air flow will be stopped, and the glycol and caustic traps will be sampled to determine the amount of iodine that penetrated the bed. The air flow will be restarted at 0.5 L/min for an additional 120 min. The air flow will be turned off and the glycol and caustic traps will be sampled to determine if any additional physiorbed iodine was removed. The iodine bed be will be removed and carefully segmented into 1–2 cm sections for neutron activation analysis (NAA).

3.5.8 **Test 8: Recirculation Iodine Sorption/Desorption and Recovery**

The objective of this test is to demonstrate the “quantitative” recovery of the injected and sorbed iodine from a recirculating air stream. The flowsheet for this test is shown in Figure 9. The iodine trap will be charged with AgA. The tritium trap section will be in place but will not contain sorbent. An air carrier gas is to be recirculated at a rate of ~0.25 L/min initially through the bypass line or empty tritium column. After the gas recirculation flow has been established for 20 min and the iodine bed is at the operating temperature of 150 °C, iodine will be introduced in the system through a charging port. The system will be operated in the “iodine” capture mode for 60–120 min by diverting the flow from the bypass line through the iodine sorbent bed. At the end of the loading period, the iodine trap will be valved out.

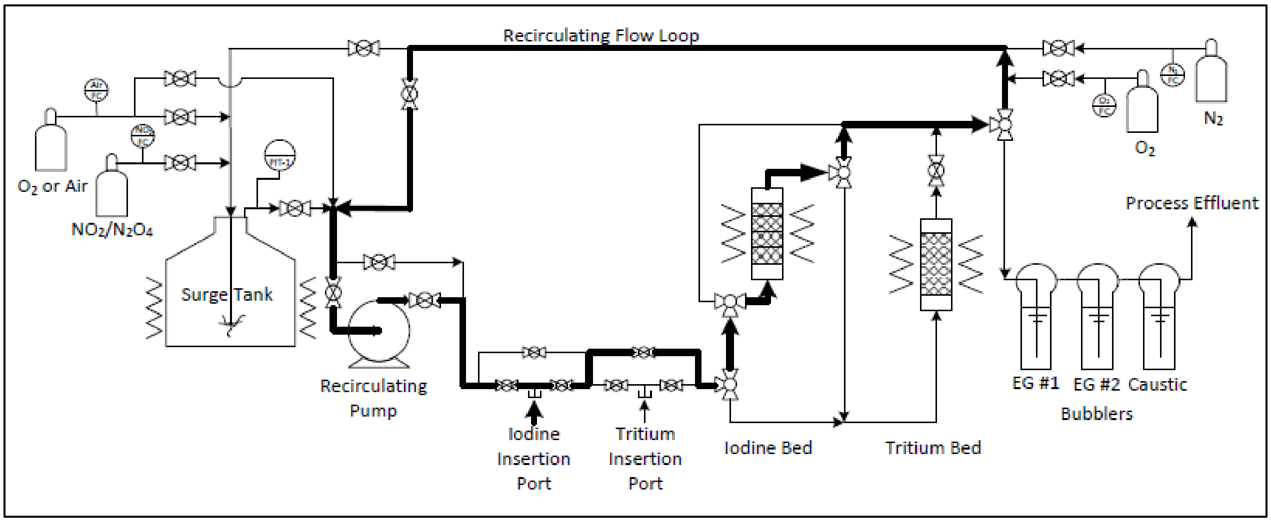

Figure 9: Schematic of iodine and tritium sorbent test system as configured for test 8.

After IC phase is complete, the recirculation pump will be stopped, and the valves will be reconfigured to bypass the pump and establish a flow path to allow the bed to be purged with air/O_2 through the glycol and caustic traps. The air flow will be established at 0.5 L/min for an additional 120 min. The air flow will be turned off, and the glycol and caustic traps will be sampled to determine if any additional physiorbed iodine was removed. The iodine bed will be removed and carefully segmented into thin sections on the order of 1–2 cm for NAA.

3.5.9 Test 9: Recirculation and Surge Tank Operation with Iodine Sorption/Desorption and Recovery from an Air Stream

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed iodine from a recirculating air stream with the surge tank in service. The flowsheet for this test is shown in Figure 10. All other aspects of this test are the same as test 8.

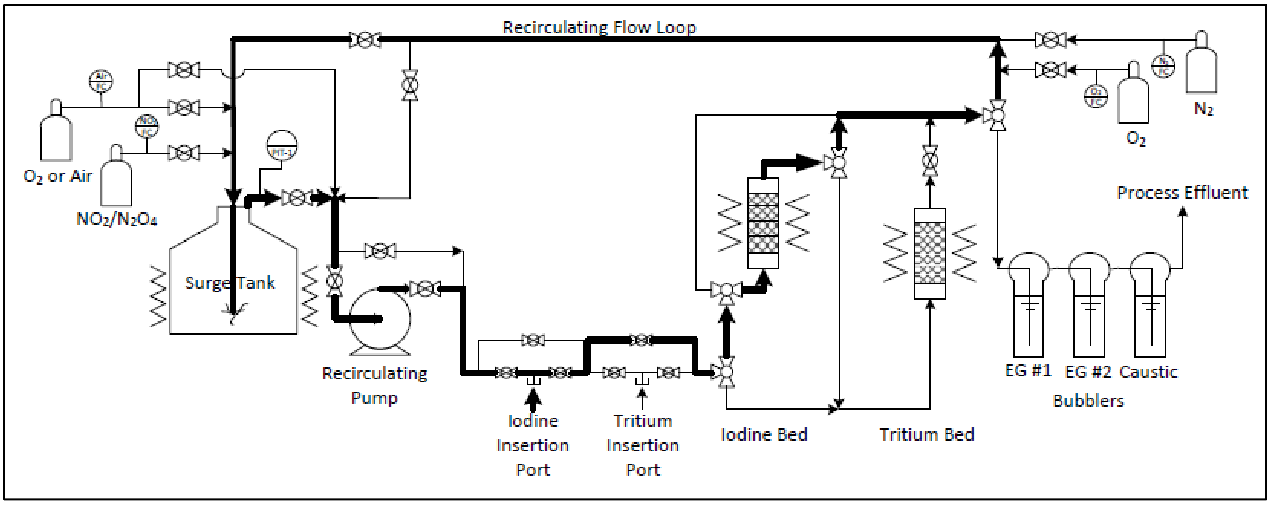

Figure 10: Schematic of iodine and tritium sorbent test system as configured for tests 9 and 10.

3.5.10 Test 10: Recirculation and Surge Tank Operation with Iodine Sorption/Desorption and Recovery from an NO_2 stream

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed iodine from a recirculating NO_2 stream with the surge tank in service. The flowsheet for this test is shown in Figure 10. This is essentially the same test as test 9 except that ~45% NO_2 is used as the carrier gas instead of the air. The charging of the NO_2 will be conducted in the same manner as test 5

3.5.11 Test 11: Once-through Iodine and Deuterium Sorption/Desorption and Recovery

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed iodine and deuterium from a once-through air stream. This is a standard air TPT off-gas system. The surge tank represents the voloxidizer. The flowsheet for this test is shown in Figure 11.

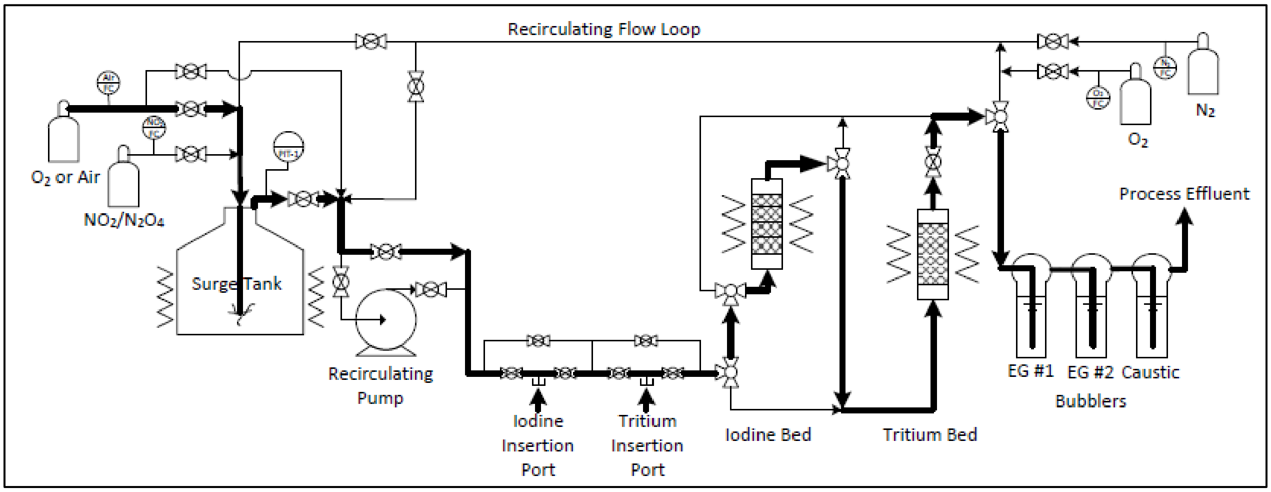

Figure 11: Schematic of iodine and tritium sorbent test system as configured for test 11.

The iodine trap will be charged with AgA. The tritium trap will be charged with silica gel. Heat the system to operating temperatures and establish an air of 0.25 L/min. Once all flows and temperatures are stable, introduce the iodine and deuterium through the injection ports. The system will be operated for 60 min. At the end of the loading period the glycol and caustic traps will be sampled and replaced. The "tritium" trap will then be desorbed through the glycol and caustic traps. The will be sampled and replaced. The iodine trap will then be desorbed / purged through the glycol and caustic traps. They will be sampled. The iodine bed will be removed and carefully segmented into thin layers of 1–2 cm sections for NAA.

3.5.12 Test 12: Iodine and Deuterium Sorption/Desorption and Recovery from a Recirculating Air Stream

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed iodine and deuterium from a recirculating air stream. This is a variant of the standard air TPT off-gas system but increases the sorbate concentrations by recirculating air/O_2. The surge tank represents the voloxidizer. The flowsheet for this test is shown in Figure 12.

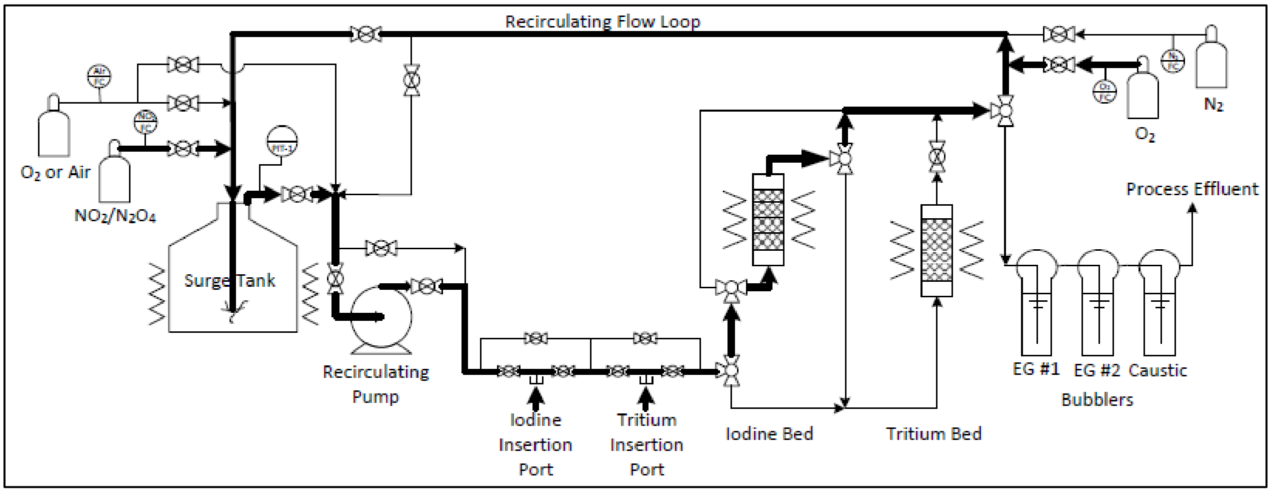

Figure 12: Schematic of iodine and tritium sorbent test system as configured for tests 12–15.

The iodine trap will be charged with AgA. The tritium trap will be charged with silica gel. Initially the tritium trap is bypassed. The system will be heated to operating temperatures and establish an air recirculation rate of 0.25 L/min. Once all flows and temperatures are stable, introduce the iodine and deuterium through the injection ports. The system will be operated in this manner for 120 min. At the end of the loading, the recirculation of the air will be stopped, and the iodine bed will be isolated. The values will be configured to route the gas flow through the tritium, glycol, and caustic traps. The system will be purged either with a 0.5 L/min flowing gas stream or by repeated pressurization of the system. The glycol and caustic traps will be sampled and replaced. The iodine trap will then be desorbed/purged the through the glycol and caustic traps. The glycol and caustic traps will be sampled. The iodine bed will be removed and carefully segmented into 1–2 cm sections for NAA.

3.5.13 Test 13: Iodine and Tritium Sorption/Desorption and Recovery from a Recirculating Air Stream

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed iodine and tritium from a recirculating air stream. This is the same as test 12 with the exception of the use of tritiated water. The flowsheet for this test is shown in Figure 12. This test should be repeated twice.

3.5.14 Test 14: Iodine and Deuterium Sorption/Desorption and Recovery from a Recirculating NO_2 Stream

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed iodine and deuterium from a recirculating NO_2 stream. This is the same as test 12 with the exception of the use of NO_2 is the carrier gas. The flowsheet for this test is shown in Figure 12.

3.5.15 Test 15: Iodine and Tritium Sorption/Desorption and Recovery from a Recirculating NO_2 Stream

The objective of this test is to demonstrate the "quantitative" recovery of the injected and sorbed iodine and tritium from a recirculating NO_2 stream. This is the same as test 14 with the exception of the use of tritium in place of deuterium. The flowsheet for this test is shown in Figure 12. The tritium trap will be charged with silica gel for test 15a and 3A MS for test 15b. Different desorption temperatures and durations will be required.

4. CONCLUSIONS

A new test bed for the advanced TPT off-gas system that addresses the issues identified in the FY 2017–2018 scoping tests has been designed. The test bed will use high nickel alloys wherever possible to address the previously observed corrosion issues, a redesigned surge tank to permit ease of purging, an improved feed system and a more modular system design that will allow testing of incremental increases in system complexity to allow the isolation of any element that results in changes to recovery of target species. Accompanying that design, a multifaceted test plan that includes a total of 15 tests with a total of 27 individual runs is described. Tests 1–5 are all performed with deuterated water as a cold stand-in for tritiated water, tests 6–10 uses iodine only, and tests 11–15 use both iodine and deuterated or tritiated water. Approximately half of the individual runs will use 40%–50% NO_2 as a carrier gas.

The data obtained will (1) demonstrate the ability of the system to capture the iodine released during TPT; (2) show any potential differences in the recoveries in the three modes of operation, and (3) indicate the extent to which the releases and recovery of both tritium and iodine can be quantified at a factional kilogram scale for TPT or ATPT demonstration.

5. REFERENCES

Johnson, J. A. and G. D. DelCul. 2016. *Reaction System Design for NO_2 Oxidation of Used Nuclear Fuel for the FY17 Hot Test*, ORNL/LTR-2016/355, UT-Battelle LLC, Oak Ridge National Laboratory, Oak Ridge, TN.

Jordan, J. A. and R. T. Jubin. 2017. *Stability of Tritium and Iodine Sorbents under Tritium-Pretreatment Off-Gas Conditions*, ORNL/SPR-2017/162, also NTRD-MRWFD-2017-000411, UT-Battelle LLC, Oak Ridge National Laboratory, Oak Ridge, TN.

Jubin, R. T., N. R. Soelberg, D. M. Strachan, and G. Ilas. 2012. *Fuel Age Impacts on Gaseous Fission Product Capture during Separations*, FCRD-SWF-2012-000089, UT-Battelle LLC, Oak Ridge National Laboratory, Oak Ridge, TN.

Jubin, R. T., S. H. Bruffey, J. A. Jordan, and G. D. DelCul. 2017. *Assembly and Testing of a Tritium and Iodine Removal System for Use with Advanced Tritium Pretreatment*, ORNL/TM-2017/464, also NTRD-MRWFD-2017-000157, UT-Battelle LLC, Oak Ridge National Laboratory, Oak Ridge, TN.

Jubin, R. T., J. A. Jordan and, S. H. Bruffey. 2018. *Testing of an Iodine and Tritium Removal System for Advanced Tritium Pretreatment Off-Gas*, ORNL/SPR-2018/15, also NTRD-MRWFD-2018-000199, UT-Battelle LLC, Oak Ridge National Laboratory, Oak Ridge, TN.

Spencer, B. B., S. H. Bruffey, J. A. Jordan, and R. T. Jubin. 2017. *Design of a Tritium and Iodine Removal System for Use with Advanced Tritium Pretreatment*, ORNL/SPR-2017/116, also NTRD-MRWFD-2017-000311, UT-Battelle LLC, Oak Ridge National Laboratory, Oak Ridge, TN.