Joint Test Plan to Identify the Gaseous By-Products of CH_3I Loading on AgZ

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign
Off-Gas Sigma Team

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November 30, 2015

ORNL/LTR-2012/604-Rev 2
FCRD-SWF-2013-000070-Rev 2
INL/EXT-12-27978-Rev 2

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This work was supported by the U.S. DOE/NE/FCT-MRWFD

Prepared for the

U.S. Department of Energy
Office of Nuclear Energy

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SUMMARY

The objective of this test plan is to describe research to determine the gaseous by-products of the adsorption of CH_3I on hydrogen reduced silver exchanged mordenite (AgZ). An initial test plan was developed in FY 2012 to discern the chemical reactions that occur when organic iodides interact with the other components in a prototypical off-gas in the presence of silver-loaded zeolite, AgZ. CH_3I is used as a surrogate for organic iodides that could be present in the gas streams, although follow-on tests include potentially using other organic iodides as well. This test plan was updated to reflect test results obtained during FY 2013 to FY 2015 and was further adjusted based on additional information from the relevant literature obtained since 2012. Four main questions are listed that need to be answered to verify earlier test results that indicate that CH_3I and I_2 are present in the effluent from a column containing AgZ.

CONTENTS

TABLES

Acronyms

AgZ	Silver exchanged mordenite
ANL	Argonne National Laboratory
APS	Advanced Photon Source
DF	decontamination factor
DOG	dissolver off-gas
DP	dew point
DRIFT	diffuse reflectance infrared Fourier transformed spectroscopy
FTIR	Fourier transform infrared spectroscopy
FY	Fiscal Year
GC/ECD	gas chromatography – electron capture detector
GC/MS	gas chromatography – mass spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
INL	Idaho National Laboratory
IR	infrared spectroscopy
ORNL	Oak Ridge National Laboratory
PDF	pair distribution function
PNNL	Pacific Northwest National Laboratory
VOG	vessel off-gas
XRF	X-ray fluorescence
GC/PID	gas chromatography/photoionization detector
MTZ	Mass transfer zone
NEUP	Nuclear Energy University Program

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

JOINT TEST PLAN TO IDENTIFY THE GASEOUS BY-PRODUCTS OF CH_3I LOADING ON AGZ

1. OBJECTIVE

The objective of this test plan is to describe research to determine the gaseous by-products of the adsorption of CH_3I on hydrogen reduced silver exchanged mordenite (AgZ).

2. BACKGROUND

In Fiscal Year 2010 (FY10), three AgZ deep bed column experiments were performed at Idaho National Laboratory (INL) in which CH_3I was the iodine source in the gas phase. During the course of these tests, elemental iodine was observed in the effluent from the bed. This was an unexpected result; on breakthrough, only CH_3I was expected. It was hypothesized that the elemental iodine was generated within the sorbent bed, presumably from a reaction sequence likely catalyzed by silver mordenite. It was also observed that the levels of CH_3I and I_2 in the effluent did not rise in concert; i.e., the ratio of the $CH_3I:I_2$ in the effluent decreased from ~96% to 3 - 5% over the course of the run (Haefner 2010).

Previous work at Pacific Northwest National Laboratory (PNNL), INL, and Oak Ridge National Laboratory (ORNL) conducted in the late 1970s and early 1980s (Jubin 1980, 1982; Murphy 1977; Scheele et al. 1983) also focused on the adsorption of CH_3I on AgZ as organic iodides were thought to pose a greater challenge to the iodine sorption media than elemental iodine. However, the speciation of the effluent from the experiments reported in the literature were not examined, or at least the results were not reported.

3. DATA GAP ANALYSIS

One key question that must be addressed initially to verify the previously observed effluent behavior is:

- Can elemental iodine in the effluent be confirmed? To answer this question requires duplicating the run from FY 2010 with sufficient sampling and analyses to confirm or refute the observations from Haefner (2010). Sub-questions include:
    a. What other iodine species are in the effluent?
    b. What organic compounds are in the effluent?

If the reported behavior is confirmed, a series of questions follow regarding the origin of the elemental iodine. These include:

- Is this a gas phase reaction between gas components?
- Is this a result of the iodine capture, i.e., a reaction between CH_3I and Ag to form AgI?
- Is this a result of a catalytic interaction between the substrate (the zeolite or the Ag on the zeolite) and the gas phase components?

Four primary technical questions have been posed as important to understand the observed behavior during the adsorption of CH_3I on AgZ at INL and are presented in Table 1. (While the phrase "adsorption of CH_3I" is used often in this document, it does not imply that we believe that CH_3I is adsorbed (physisorbed or chemisorbed) as CH_3I. The interest is in capturing iodine, and it is believed that the methyl group is cleaved and the iodine is captured mainly as AgI.) The relevant past work (nuclear and non-nuclear related) and possible approaches to develop answers to the four main questions is shown in Table 1. No attempt has been made to make the list reflect an exhaustive literature search. Selected results of tests performed since 2012 to address the questions are also listed.

Additional questions related to the iodine capture performance of the sorbent for streams containing CH_3I are shown in Table 2. The answers to these four questions in Table 2 allow comparisons between results from iodine capture experiments with elemental iodine and CH_3I.

The test plan presented below details the Phase I tests needed to identify the gaseous by-products that arise from the reaction of CH_3I on AgZ. The subsequent phases are needed to address the remaining questions and are included for completeness, but in less detail. The completion of all phases is needed to gain fundamental engineering data associated with the adsorption of organic iodide compounds on silver-containing sorbents.

Table 1. Methyl iodide adsorption behavior and questions pertaining to the reaction products and effluents

Phenomenon or question (and initial answers based on FY13-FY15 work)[1]	Priority[2]	Initial answers/comments from past work prior to 2012	Answers from recent (FY13-FY15 work) or proposed options to address the questions
1-1. What happens to organic iodide? What is the mechanism? a. React in gas stream prior to interaction with solid sorbent? (Not significantly based on research since 2012.) - Impact of NO, NO_2, H_2O, O_2. (Evaluation with H_2O up to 1.9 vol%, NO+NO_2 up to 2000 ppm, and HNO_3 up to 9600 ppm is complete since 2012.) b. React because of interaction with solid sorbent? (Yes per tests since 2012.) - Impact of NO, NO_2, H_2O, O_2. (Evaluation with H_2O up to 1.9 vol%, NO+NO_2 up to 2000 ppm, and HNO_3 up to 9600 ppm is complete since 2012.) - Impact of the solid sorbent – Ag catalytic? Different sorbents? (Initial evaluation with AgZ and AgAero has been done since 2012; not yet done for mordenite or aerogel in the absence of Ag.) c. Iodine is separated from organic moiety after physisorption prior to chemisorption? (A mechanism has been proposed based on work since 2012) d. Iodine is not separated from organic moiety? (No – iodine is separated from organic moiety based on work since 2012.)	C C M M	Thermodynamically, CH_3I more favorably reacts with Ag to form AgI in the presence of NO than in the presence of NO_2; NO improves trapping efficiency as does water (Scheele et al. 1983); {Note: this is not consistent with statement from Scheele 1983 below in Question 1 in Table 2 about NO}; Scheele et al. (1983) also found experimental conditions in which both CH_3I and I_2 appeared in the effluent at breakthrough. CH_3I converted to I_2 such that the determination of capture efficiency of total iodine must account for both CH_3I and (I_2+HI) in the effluent gas. At initial breakthrough, most (95%) of the small amount of breakthrough is due to CH_3I; but as breakthrough continues and efficiency decreases, the amount of breakthrough (I_2+HI) rises faster than the amount of breakthrough CH_3I, reaching 97% of total iodine breakthrough (Haefner 2010). Sakurai and coworkers (1984) found that CH_3I and NO_2 did not react, but required the presence of zeolite with or without Ag to be present. The reaction yielded CH_3NO_3 and I_2. Sakurai and Takahashi (1994) found that Ag-impregnated silica (AgS) acted as a catalyst for the decomposition of CH_3I in the presence of NO_2 even after all the Ag had reacted. This has implications for the ratio of organic and inorganic iodine as breakthrough occurs and can lead to an over estimation of the sorbent capacity. Parsley (1971) published an extensive review of the chemistry of CH_3I. He lists a sequence of reactions published by Ogg (1934) in which I_2 is generated from the reaction sequence. The thermal decomposition of CH_3I at <320 °C is negligible in the absence of a catalyst. Murray and coworkers (1994) did work with alkali-exchanged faujasites. As part of their conclusions they indicate that the adsorbed product would be oxidized to form the final product and the elemental halide that was needed to make the organic halide needed to start the overall reaction sequence. Parsley (1971) points out that Senter (1910) found that AgI acted as a catalyst for the reaction between alkyl halides and the silver salts.	CH_3I does not significantly react in the gas phase with other gas species for the test conditions based on ORNL HSC Chemistry modeling and results (Soelberg 2014a, 2014b, 2014c, and 2015). Less than 4.7% conversion of CH_3I to I_2 or HI was measured. Tests showed that CH_3I does react with the AgZ and Ag aerogel. This reaction and reaction products vary depending on presence or lack of H_2O and NO_x (Soelberg 2014a, 2014b, 2014c, and 2015). Iodine is separated from the organic moiety through interactions with AgZ and Ag aerogel, and has been detected in significant quantities as I_2 or HI (the caustic scrubbing and ICP-MS analysis does not discriminate between I_2 and HI) (Nenoff 2014, Soelberg 2104a, 2014b, 2014c, and 2015). A mechanism that describes separation of iodine from the organic moiety after physisorption has been proposed (Nenoff 2014). However, a review of the literature suggests that the reactions may be more complex. Scheele et al. (1983) show that thermodynamically NO_x can cause liberation of I_2 from AgI. Deep-bed tests continue w/ CH_3I, I_2,HI gas analysis, w/ and w/o Ag (INL).

Table 1. Methyl iodide adsorption behavior and questions pertaining to the reaction products and effluents

Phenomenon or question (and initial answers based on FY13-FY15 work)[1]	Priority[2]	Initial answers/comments from past work prior to 2012	Answers from recent (FY13-FY15 work) or proposed options to address the questions
1-2. What is ultimate fate of the organic moiety? a. Adsorbs onto sorbent? As what species? (Gravimetric analysis of spent sorbent since 2012does not indicate quantitative adsorption of by-product organic species onto the sorbent.) b. Is released or remains in gas stream? What species? (Yes, various organic species, but not enough to quantitatively account for all of organic moiety, according to work since 2012.)	 L M	Donner and Tamberg (1971) proposed CH_3OH (methanol) and CH_3OCH_3 (dimethyl ether) as possible organic reaction products as do Scheele et al. (Scheele et al. 1983). Dimethyl ether detected at outlet (prior work cited in Scheele). Lazo et al. showed that CO, CO_2, and CO_3^{2-} were possible reaction products albeit on a different metal catalyst system. These products formed from the reactions on a hydrated Al_2O_3 surface (metal catalyst support). Su et al. (Su et al. 2000a,b, 2004, and 2006) studied the reactions of CH_3I on single crystal and powdered TiO_2 with and without a monolayer of Ag^0. The reaction products in the presence of O_2 were $CH_2O(g)$, $Me_2O(g)$, CO(g), $CO_2(g)$, and $H_2O(g)$. [Some of these organic gas components were also noted by Scheele et al (1983).] In the absence of Ag, CH_3I decomposed to adsorbed I and CH_4. The presence of surface hydroxyl groups is necessary. In the presence of Ag and no O_2, the reactions yielded C_2H_6, while with O_2, the above listed organics were found. GC peak matched retention time of methanol (Haefner 2010).	Depending on gas matrix and sorbent, methanol, dimethyl ether, methyl nitrite and/or nitromethane (both have chemical formula CH_3NO_2, but they have different chemical structures), methyl nitrate, acetic acid, iodonaphthaline, and 3-amino 1-propanol have been tentatively detected, but not consistently and not in high enough amounts to account for all of organic moiety (Nenoff 2014, Soelberg 2014b, Soelberg 2014c, 2015). Other possible gaseous C and H species not yet analyzed include CO, CO_2, H_2O, and H_2. Deep-bed tests continue – GC, MS analysis of gas, mass of sorbent, ultimate analysis of sorbent (INL). Methods to determine small amounts of by-product adsorption on the sorbent will be evaluated.
1-3. What is the form of iodine on the sorbent material? a. AgI b. Other species c. Physisorbed vs. chemisorbed and different forms of physisorption – surface vs. pore, etc. (Primarily chemisorbed iodine, but surface vs. pore, etc. has not been determined.)	 H H H	AgI or $AgIO_3$ based on thermodynamic equilibrium, possibly a silver-iodine complex speculated based on empirical results (Scheele et al. 1983). (But the empirical results could also be explained by physisorption and desorption of a portion of the total iodine.) In the literature, the iodine from CH_3I sorbed or reacted with the Ag. Parsley (1971) points out that Senter (1910) found that AgI acted as a catalyst for the reaction between alkyl halides and the silver salts. The hydrolysis of alkyl halides increased by several orders of magnitude in the presence of silver salts.	Test results show that, analogous to I_2 adsorption, the iodine from CH_3I is primarily chemisorbed as Ag and I species, and very little is physisorbed because the amounts of iodine removed during post-test air purging of spent sorbent has been low, ranging up to ~4% (Soelberg 2014a, 2014b, 2014c, and 2015).
1-4. Does the proposed mechanism explain the observed changes in effluent composition with time?	C		

1) The comments shown in () are the terse summaries of the work carried out from FY 2013 to FY 2015.

2) Priority codes: C = Critical; H = High; M = Medium; L = Low

Table 2. Methyl iodide adsorption behavior and questions pertaining to iodine capture performance

Phenomenon or question (and initial answers based on FY13-FY15 work)	Priority[1]	Initial answers/comments from past work	Answers from recent (FY13-FY15 work) or proposed options to address the questions
2-1. What are potential adsorption efficiencies and mass transfer zone depths for organic iodide? - Impact of NO, NO_2, H_2O, O_2	C	Trapping efficiency higher with H_2O and no NO (Scheele 1983). CH_3I capture efficiency: No impact of O_2, improves at higher T from 100-200 °C, improves at higher H_2O from to 0.01-1.2 vol %; (prior work cited in Scheele 1983).	Deep-bed tests and data evaluation still in progress. Several AgZ and one Ag aerogel tests have been completed, more are planned for FY15 and beyond. A series of thin bed tests using a statistical designed set of experiments is under way at ORNL to evaluate the effects of these constituents. Both AgZ and AgAero are being evaluated.
2-2. What are potential adsorption capacities and Ag utilizations for organic iodide for base case AgZ and Ag-functionalized Aerogel (AgAero) - Impact of NO, NO_2, H_2O, O_2 on AgZ (Tests performed so far show a practical maximum adsorption capacity ranging from 5-10 wt% (g adsorbed I per 100 g original sorbent [~33-75% Ag utilization) for NO+NO_2 levels up to 1600 ppm; decreased to 6 wt% for 2000 ppm NO+NO_2 [51% Ag utilization].) - Impact of NO, NO_2, H_2O, O_2 on Ag-functionalized Aerogel (Only 1 AgAero test done so far; 26.2 wt% iodine loading, 50.4% Ag utilization.)	H L	Potential maximum capacities and Ag utilizations were not demonstrated by Scheele et al. (1983), Haefner (2010), Jubin (1980, 1982), or Murphy (1977) because those tests stopped at or shortly after an arbitrary decrease in sorption efficiency (DF = 1000 for Jubin 1980 or 1982; DF = 100 for Scheele 1983; 250 ppb CH_3I in effluent stream for Haefner 2010). NO improves I_2 loading; NO_2 decreases I_2 loading; water up to 5.5 vol% has negligible effect on loading; Temp between 100-250 °C has negligible effect on loading (Murphy 1977). CH_3I at ~170 ppmv; No impact of NO or NO_2 on CH_3I loading; H_2O up to 4.8 vol% improves CH_3I loading; T up to 225 °C improves loading but also increases depth of MTZ (Jubin 1980, 1982). CH_3I at ~300 ppm; NO, NO_2 at 0, ~1000, and ~20,000 ppm; H_2O at 0.01% and 1.2%; used on-line gas chromatography/photoionization detector (GC/PID) for measuring CH_3I; starch to indicate I_2 presence; measured iodine in sorbent with X-ray fluorescence (XRF). Iodine capacities measured up to 21.7 wt% (Scheele 1983). CH_3I at 25-34 ppm; 500-800 ppm NO, NO_2; 1.5-2% H_2O; 150 °C; 4.3 m/min superficial velocity; 5.5-7.1% iodine loading. On-line GC/ECD detection of CH_3I, iodine loading determined gravimetrically (Haefner 2010). Sakurai and coworkers (Sakurai et al. 1984) found that CH_3I and NO_2 did not react, but required the presence of zeolite with or without Ag. The reaction yielded CH_3NO_3 and I_2. The same reaction was found for C_2H_5I. In dry air at temperatures >100 °C, they found that zeolite 13x did not sorb NO_2 but did sorb I_2. With	Work in progress: 1. Deep-bed tests – several AgZ, 1 Aerogel, selected gas conditions (Soelberg 2014a, 2014b, 2014c, and 2015). 2. A series of thin bed tests using a statistical designed set of experiments is under way at ORNL to evaluate the effects of these constituents. Both AgZ and AgAero are being evaluated. 3. Aerogel tests (PNNL). Determine base case AgZ (ORNL) and base case Ag-functionalized Aerogel (PNNL).

Table 2. Methyl iodide adsorption behavior and questions pertaining to iodine capture performance

Phenomenon or question (and initial answers based on FY13-FY15 work)	Priority[1]	Initial answers/comments from past work	Answers from recent (FY13-FY15 work) or proposed options to address the questions
		water present, the zeolite loses the ability to sorb I_2.	
2-3. Kinetic data (effective diffusivity)	M		A series of thin bed tests using a statistical designed set of experiments is under way at ORNL to evaluate the effects of these constituents. Both AgZ and AgAero are being evaluated.
2-4. How do adsorption efficiencies, mass transfer zone, capacities, and Ag utilization vary for: a. Different AgZs and Aerogels – structures, elements, Ag levels, surface areas / pore structures b. Reduced vs. non-reduced and method of reduction c. Different aging of Ag-reduced sorbents d. Different sorption T, superficial velocity	M H M H	a. Smaller [20-40 mesh (0.042-0.0841 cm)] better than larger [0.16 cm extrudate] particles (Scheele et al. 1983) b. Ag^oZ better than AgZ (Scheele et al. 1983, Thomas 1977); Ag^oZ 2× higher capacity than AgZ, up to 17.1% I_2 loading at DF=1000 (Murphy 1977, Thomas 1977); 12.7 wt% for CH_3I (Jubin 1980, 1982). Higher reducing T from 200-500 °C and longer times up to 48 h increase size of Ag nodules and reduce loading capacity; but partially exchanged Ag^oZ increased Ag utilization (presumably due to smaller Ag nodules?) (Jubin 1980 or 1982). c. Aging decreases I_2 sorption capacity of H-reduced AgZ (Bruffey 2012, Jubin 2012). d. Temperatures up to 200 °C and lower velocities down to 3.75 m/min improve trapping efficiency (Scheele 1983).	Work in progress and future work: 1. Capacities for different AgZs, H-reduction, aging, and T (ORNL thin-bed tests). 2. Capacities for different Aerogels, H-reduction, aging, and T (PNNL tests). Constant superficial velocity; limit variation in zeolites and Aerogels. How should experiments address aging of reduced sorbents during long test?

1) Priority codes: C = Critical; H = High; M = Medium; L = Low

4. TEST PLAN

Phase II and potential follow-on tests are less well-defined and will be revised and refined based on a review of the Phase I test results. Conceptually, the Phase II portion of this test plan is designed to provide significantly more insight into the mechanisms associated with the adsorption and reaction or decomposition of CH_3I and other organic iodides on AgZ and other iodine sorbents, but is not envisioned as an all-inclusive test plan for all sorbents and organic iodides. These tests should provide data to support engineering calculations that are needed to design iodine capture systems that efficiently and reliably remove organic iodides.

Note: Question numbers follow specific test numbers shown in Table 1 and Table 2.

1. Phase I Testing – Confirm previous observations and identify primary factors.
    a. Chemical equilibrium calculations – HSC Chemistry or some other model – of what might be expected in gas-phase and gas-solid phase reactions (ORNL to do gas–gas reactions.) (questions 1-1, 1-2b) (Done)
    b. Deep-Bed Tests at INL
        i. Determine stability of gas phase samples that contain methyl iodide. (Done. Gas samples in Tedlar bags, Mylar bags, and glass sample tubes, with and without shielding from light, are inconsistently unstable. Either on-line or rapid analysis (<1 h hold times) of grab samples is recommended [Soelberg 2014c]).
        ii. Blank tests – CH_3I and no sorbent, 150 °C, with and without NO, NO_2, H_2O, to assess gas-phase reactions. These tests are performed with gas phase only – no sorbent in columns (Question 1-1a). (Partially complete. Results are summarized in Table 1. Yet to do: A blank test with NO and NO_2 concentrations up to 10,000 ppm each.)
            1. Test 1:
                a. 150 °C,
                b. superficial velocity 4.3 m/min,
                c. 33 ppm CH_3I,
                d. 6,000 ppm water (0 °C Dew Point [DP]),
                e. Up to 10,000 ppm NO,
                f. Up to 10,000 ppm NO_2.
            2. Test 2 – if elemental iodine is observed in Test 1 in this series, perform a test without H_2O and NO_x: (Done, see Table 1.)
                a. 150 °C,
                b. superficial velocity 4.3 m/min,
                c. 33 ppm CH_3I,
                d. ~10 ppm water (DP −60 to −70 °C),
                e. 0 ppm NO,
                f. 0 ppm NO_2
            3. Test 3 – if elemental iodine is observed in Test 1 in this series at the higher NOx levels, perform a test without H_2O at the higher NO_x levels. Done, see Table 1.)
                a. 150 °C,

        b. superficial velocity 4.3 m/min,
        c. 33 ppm CH_3I,
        d. ~10 ppm water (DP −60 to −70 °C),
        e. 10,000 ppm NO,
        f. 10,000 ppm NO_2
    4. Inlet and outlet gas streams will be analyzed to measure CH_3I, I_2, and to the extent practical with existing available instrumentation, other likely gaseous reaction products, such as CO and CO_2, in near real time using Fourier transform infrared spectroscopy (FTIR), gas chromatography-mass spectrometry (GC-MS), inductively coupled plasma mass spectrometry (ICP-MS).
    5. Evaluate the tramp halide contribution in the test gases to ensure these are not influencing factors. If these are not present at detectable levels, then this effect should be considered in later tests.

iii. Replicate CH_3I loading on deep bed to confirm presence of elemental iodine in effluent. Goal: Determine presence/absence of I_2 and/or CH_3I at intermediate points in the bed. First branch point: Is I_2 observed? If no, then the primary purpose of this test plan has been achieved. (Question 1-1b, 1-1c) (Done.)
    1. Test 1:
        a. 150 °C,
        b. superficial velocity 4.3 m/min,
        c. 33 ppm CH_3I,
        d. ~6,000 ppm water (DP 0 °C) to 2 wt% water (DP ~18 °C)
        e. 833 ppm NO,
        f. 833 ppm NO_2.

        (Two tests bracket the above conditions:

        CH_3I-4: 18,000 ppm H_2O and 824 ppm each for NO and NO_2, 57 ppm CH_3I. Measureable quantities of inorganic iodine were detected downstream of AgZ bed.

        CH_3I-12: 0.3 ppb H_2O, 1000 ppm each NO and NO_2, 45 ppm CH_3I, and 165 °C; Measureable quantities of inorganic iodine were detected downstream of AgZ bed.)

    2. Test 2 – If I_2 is observed in Test 1 in this series, perform a test without H_2O and NO_x: (Done.)
        a. 150 °C,
        b. superficial velocity 4.3 m/min,
        c. 33 ppm CH_3I,
        d. ~10 ppm water (DP −60 to −70 °C),
        e. 0 ppm NO,
        f. 0 ppm NO_2

(CH$_3$I-5. A deep-bed test was completed with target concentrations of ~30 ppm H_2O and 0 ppm NO and NO_2 with AgZ. Measureable quantities of inorganic iodine were detected downstream of AgZ bed.)

3. Test 3 – If elemental iodine is observed in Test 1 in this series, perform a test without H_2O: (Done.)
    a. 150 °C,
    b. superficial velocity 4.3 m/min,
    c. 33 ppm CH_3I,
    d. ~10 ppm water (DP −60 to −70 °C),
    e. 833 ppm NO,
    f. 833 ppm NO_2

    (CH$_3$I-6. A deep-bed test was completed with target concentrations of ~30 ppm H_2O and 833 ppm each for NO and NO_2 with AgZ. Measureable quantities of inorganic iodine were detected downstream of AgZ bed. Future deep-bed tests can be adjusted to the above target conditions.)

4. Test 4 – Added test at higher temperature and NO_x concentrations: (Done.)
    a. 165 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I,
    d. ~10 ppm water (DP −60 to −70 °C),
    e. 1000 ppm NO,
    f. 1000 ppm NO_2

    (CH$_3$I-12: 0.3 ppb H_2O, 1000 ppm each NO and NO_2, 45 ppm CH_3I, and 165 °C; significant I_2/HI was detected downstream of AgZ bed.)

5. Inlet and outlet gas streams should be analyzed to measure CH_3I, I_2, and to the extent practical with existing available instrumentation, other likely gaseous reaction products such as CO, CO_2, HI, CH_2O, $(CH_3)_2O$, H_2O, CH_3NO_2, in near real time with available tools including FTIR, GC-MS, ICP-MS.
6. Examine the sorbent at the end of the run for total carbon adsorbed on the surface or in the sorbent.
7. Determine if there are temporal changes in form; that is, does I_2 at a given distance in the bed increase with run time, or is it fixed with respect to adsorption front? This may require a slight change in design of the deep bed system, such as six 1.27 cm deep beds instead of beds of varying depth. The actual configuration should be developed following assessment of results of the initial tests.

iv. Repeat tests with different configurations of the sorbent to determine if effect detected in 1.a is a result of the presence of Ag, Ag compounds (atomic O dissolved in the Ag and AgI), or merely the result of the substrate. Goal: Determine if observed behavior is the same or different as with AgZ. (Question 1-1b, 1-1c)

1. Repeat tests 1.b.iii 1 and 1.b.iii.2 with four substrates (1) HZ, (2) NaZ[a], (3) unreduced AgZ, (4) fully iodine reacted AgZ (i.e., AgI-Z). The use of reduced AgZ that has not come in contact with air, and where only nitrogen is used as the carrier gas should be considered for a potential follow-on test to evaluate the roll of oxygen. If an effect is observed in test 1.b.iii.1, conduct the follow-on test 1.b.iii.2 with alternate zeolite. Initial results might be obtained in static tests followed by dynamic tests with configurations selected from the static tests.

v. Characterize the form/species of iodine in the gas stream that passes between bed sections. (Questions 1-1c, 1-2b)

1. Sample analysis techniques, including FTIR, GC, ICP-MS, have been used in the past. However, there are several other techniques available that have been used when examining the behavior of iodine species in the atmosphere, such as cryogenic concentration and purge and trap gas chromatography. In the atmosphere, the organic iodine species are measured in the low parts per billion, concentrations that are orders of magnitude below those found in process off-gas streams and in the range expected downstream from iodine removal processes. These techniques should be investigated.

c. Thin-bed (single pellet deep) tests at ORNL. The thin bed tests are conducted in a bed that is effectively one pellet deep. Thus, all pellets are exposed to the same gas stream composition, and the gas composition is virtually unaffected by the adsorption. These tests will utilize the test protocol established in the joint test plan for thin bed and deep bed testing of iodine sorbents (Jubin 2012b). A portion of the materials produced in this series of tests will be used in the analysis performed in Section 1.d of this plan.

i. General test conditions to be used on this series of tests:

1. Test 1: (Effects of water and NO_x)
    a. 165 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I or 25 ppm I_2,
    d. ~6,000 ppm water (DP 0 °C),
    e. 1000 ppm NO,
    f. 1000 ppm NO_2.
2. Test 2: (Effects of NO_x only)
    a. 165 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I,

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[a] Murry and coworkers (Murray et al. 1993) observed differences in the catalytic activity of alkali-bearing zeolites, with the Na form having the highest catalytic activity. This is the reason for studying both the H and Na forms.

    d. ~10 ppm water (DP −60 to −70 °C),
    e. 1000 ppm NO,
    f. 1000 ppm NO_2.
3. Test 3a: (Effects of no water and no NO_x)
    a. 165 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I,
    d. ~10 ppm water (DP −60 to −70 °C),
    e. 0 ppm NO,
    f. 0 ppm NO_2.
4. Test 3b: (Temperature effects)
    a. 135 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I,
    d. ~10 ppm water (DP −60 to −70 °C),
    e. 0 ppm NO,
    f. 0 ppm NO_2.
5. Test 3c: - (Test temperature effects)
    a. 150 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I,
    d. ~10 ppm water (DP −60 to −70 °C),
    e. 0 ppm NO,
    f. 0 ppm NO_2.
6. Test 4: (Test matches initial INL deep bed test condition)
    a. 150 °C,
    b. superficial velocity 4.3 m/min,
    c. 33 ppm CH_3I,
    d. ~10 ppm water (DP −60 to −70 °C),
    e. 0 ppm NO,
    f. 0 ppm NO_2.
7. Test 5: (Test 1% NO_x effects)
    a. 165 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I,
    d. ~10 ppm water (DP −60 to −70 °C),
    e. 10,000 ppm NO,
    f. 10,000 ppm NO_2.
8. Test 6: (Test NO_2 and water combined effects)
    a. 165 °C,
    b. superficial velocity 4.3 m/min,
    c. 50 ppm CH_3I,
    d. ~6,000 ppm water (DP 0 °C),

            e. 0 ppm NO,
            f. 10,000 ppm NO_2.
        9. Test 7: (Confirm non-effect of superficial velocity)
            a. 165 °C,
            b. superficial velocity 10 m/min,
            c. 50 ppm CH_3I,
            d. ~6,000 ppm water (DP 0 °C),
            e. 0 ppm NO,
            f. 0 ppm NO_2.
    d. Structural studies, pair distribution function (PDF), or alternate studies at Argonne National Laboratory/Advanced Photon Source (ANL/APS) or elsewhere will be performed on samples prepared at INL and Oak Ridge National Laboratory (ORNL). The goal is to determine if the adsorption of CH_3I (or adsorption of I from CH_3I) occurs at the same sites as I_2. This could be part of a potential Nuclear Energy University Program (NEUP) project.
        i. Static tests to see where CH_3I adsorbs on AgZ (question 1-3c)

2. Phase II Testing – Since the results from Phase I tests performed to date confirm the presence of both I_2 and CH_3I in the gaseous effluent from the AgZ, the additional testing shown here is justified. In this phase, more in-depth tests for selected conditions will be conducted to build upon the point studies conducted in Phase I. Some of these tests may or may not need to be performed depending on the results obtained from Phase I tests.
    a. Deep bed tests at INL
        i. Determine decontamination factor (DF) – how is this affected by operating conditions for CH_3I adsorption.
        ii. Determine mass transfer zone (MTZ) – how is this affected by operating conditions for CH_3I adsorption.
        iii. Tests with CH_3I and mixtures of CH_3I, I_2, and HI at prototypic dissolver off-gas (DOG) concentrations and higher concentrations
            1. Characterize the gases passing between bed sections
            2. Characterize the solids after reactions have run their course
        iv. Tests with wider range of CH_3I concentrations. There is literature to suggest that the kinetics are faster at low concentrations and that other, more complicated, reactions become dominant at higher concentrations
    b. Thin bed tests at ORNL
            1. Determine the maximum capacity for CH_3I and mixtures of organic and inorganic iodine
                a. Impact of H_2O, NO, NO_2 on CH_3I adsorption. (question 1-1b, 2-1, 2-2, 2-3, 2-4)
                b. Determine the effects on the solid sorbent
        ii. Tests with wider range of CH_3I concentrations. There is literature to suggest that the kinetics are faster at low concentrations and that other, more complicated, reactions become dominant at higher concentrations.

   c. Studies on AgZ with variations in streams to monitor sorption in real time (CH_3I, H_2O, NO, NO_2, etc.) with in situ diffuse reflectance infrared Fourier transform (DRIFT)/PDF [infrared (IR) & synchrotron]
      i. Impact of H_2O, NO, NO_2 on CH_3I adsorption. (questions 1-3c and 2-2)
   d. Structural studies (PDF) or alternate studies at ANL/APS or elsewhere on samples prepared at INL and ORNL. Goal is to identify if the adsorption of CH_3I (or adsorption of I from CH_3I) occurs at the same sites as I_2. This could be part of a potential NEUP project.
      i. Static tests to see where CH_3I adsorbs on AgZ (question 1-3c)

3. Potential follow-on Testing –
   a. Conduct a scoping series of tests following a similar plan as described above for Phase I and Phase II to evaluate the CH_3I capture on silver functionalized silica aerogel and other candidate iodine sorbent materials.
   b. Conduct a series of tests using deuterium or carbon-13 labeled organic iodides to aid the tracking of reaction products.
   c. Evaluate the potential displacement of I with tramp halides that could be introduced in the cold chemical streams and in test gases.
   d. Conduct deep bed tests with inorganic iodine (I_2 HOI, HI, and ICl) to determine a set of reference data. Iodic acid could be considered if and when the need is established and a suitable generator is available.
      i. Ag-free sorbent (the form to be determined from the results of Phase I tests with HZ and NaZ)
      ii. Ag-loaded sorbent
      iii. AgI-loaded sorbent
      iv. More possible test parameters:
         1. NO, NO_2 each up to 10,000 ppm
         2. Calculate the HNO_3 based on vapor pressure of HNO_3 at about 0-20 °C, and/or expected remaining aerosols in DOG downstream of condenser and demister.
         3. Deepest bed practical – 0.5 to 1 m
         4. Add other organic iodides like iodododecane
         5. Vary temperature
   e. Expanded evaluations into prototypic conditions for DOG and vessel off-gas (VOG)
   f. Ag-aerogel and AgZ; Aerogel at higher NO_x especially. Need to develop separate test plan for Ag-aerogel – at least conduct a scoping study; i.e., suitably modified Phase I tests 1 and 2, early to see if behavior is similar.
   g. The effect of light on the stability CH_3I in the feed stream or other approach to change form of organic iodide; i.e., can we degrade the CH_3I to I_2, prior to where iodine adsorption would be done in a DOG system.
   h. For the materials that meet the minimums above, perform tests at INL and ORNL with prototypic gas mixtures (air, humidity, mixtures of NO_x, other off-gas components)
      i. Perform deep-bed tests at INL with prototypic gas streams containing iodine species and concentrations that are likely to be found in the reprocessing facility
         1. Characterize the solids from these tests

        2. Characterize the changes in the component concentrations in these prototypic gases when they pass through the solid sorbent; Ag-free sorbent
    ii. Perform capacity tests at ORNL with prototypic gas streams containing iodine species and concentrations
        1. Characterize the solids from these tests
        2. Characterize the changes in the component concentrations in these prototypic gases when they pass through the solid sorbent; Ag-free sorbent
    iii. Perform 'aging' tests at ORNL with prototypic gas streams
        1. Characterize the solids from these tests
        2. Characterize the changes in the component concentrations in these prototypic gases when they pass through the solid sorbent; Ag-free sorbent

4. Question / Test crosswalk

Table 3 is a crosswalk between the questions posed in Tables 1 and 2 with the specific tests conducted to provide insight.

Table 3. Crosswalk between questions posed by this test plan and planned tests to address questions

Questions	Tests
1-1. What happens to organic iodide? What is the mechanism?	
a. React in gas stream prior to interaction with solid sorbent? (Not significantly)	1.a, 1.b.ii
b. React because of interaction with solid sorbent? (Yes)	1.b.iii, 1.b.iv, 2.b.1.a
c. Iodine is separated from organic moiety after physisorption prior to chemisorption? (proposed mechanism for separation after physisorption)	1.b.iii, 1.b.iv, 1.b.v, 1.c.ii.2, 1.c.ii.4, 2.c.i
d. Iodine is not separated from organic moiety? (no – iodine is separated from organic moiety)	1.c.ii.2, 1.c.ii.4
1-2. What is ultimate fate of the organic moiety?	
a. Adsorbs onto sorbent? As what species? (Gravimetric analysis of spent sorbent does not indicate adsorption of byproduct species onto the sorbent.	1.a, 1.b.v
b. Is released or remains in gas stream? What species?	
1-3. What is the form of iodine on the sorbent material?	1.c.ii.2, 1.c.ii.4
a. AgI	
b. Other species	
c. Physisorbed vs chemisorbed and different forms of physisorption – surface vs pore, etc. (Primarily chemisorbed iodine, but surface vs. pore, etc., has not been determined.)	1.d, 2.d.i
1-4. Does the proposed mechanism explain the observed changes in effluent composition with time?	1.a-1.d; 2.a-2.d; 3.a-3.f
2-1. What are potential adsorption efficiencies and mass transfer zone depths for organic iodide? - Impact of NO, NO$_2$, H$_2$O, O$_2$	2.b.1.a
2-2. What are potential adsorption capacities and Ag utilizations for organic iodide for base case AgZ and Ag-functionalized Aerogel?	2.b.1.a, 2.c.i
2-3. Kinetic data (effective diffusivity)	1.c.ii.2, 1.c.ii.4, 2.b.1.a
2-4. How do adsorption efficiencies, mass transfer zone, capacities, and Ag utilization vary for:	2.b.1.a
a. Different AgZs and Aerogels – structures, elements, Ag levels, surface areas / pore structures	
b. Reduced vs non-reduced and method of reduction	
c. Different aging of Ag-reduced sorbents	
d. Different sorption T, superficial velocity	

5. Conclusions

A test plan was developed in FY 2012 to discern the chemical reactions that occur when organic iodides interact with the other components in a prototypical off-gas in the presence of silver-loaded zeolite, AgZ. CH_3I is used as a surrogate for organic iodides that could be present in the gas streams, although follow-on tests include potentially using other organic iodides as well.

This test plan was updated to reflect test results contained during FY 2013 to FY 2015 and was further adjusted based on additional information from the relevant literature obtained since 2012. Four main questions are listed that need to be answered to verify earlier test results that indicate that CH_3I and I_2 are present in the effluent from a column containing AgZ, and to evaluate how the ratio of CH_3I to I_2 changes with time at column breakthrough (Table 1).

Relative to previous tests, additional instrumentation and analyses are suggested for future tests to better determine the fate of the organic part of CH_3I. Results from some of the scoping tests may suggest that some of the suggested future tests need not be performed or that other tests may be needed. The expected outcome of the tests performed under this test plan is at least a qualitative understanding for the presence of CH_3I and I_2 in changing amounts in the effluent from an AgZ column.

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