Initial Evaluation of Effects of NO_x on Iodine and Methyl Iodide Loading of AgZ and Aerogels

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S. H. Bruffey and R. T. Jubin
Oak Ridge National Laboratory

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SUMMARY

This initial evaluation provides insight into the effect of NO on the adsorption of both I_2 and CH_3I onto reduced silver-exchanged mordenite (Ag^0Z). It was determined that adsorption of CH_3I onto Ag^0Z occurs at approximately 50% of the rate of I_2 adsorption onto Ag^0Z, although total iodine capacities are comparable. Addition of 1% NO to the simulated off-gas stream results in very similar loading behaviors and iodine capacities for both iodine species. This is most likely an effect of CH_3I oxidation to I_2 by NO prior to contact with the sorbent bed. Completion of tests including NO_2 in the simulated off-gas stream was delayed due to vendor NO_2 production schedules. A statistically designed test matrix is partially completed, and upon conclusion of the suggested experiments, the effects of temperature, NO, NO_2, and water vapor on the sorption of CH_3I and I_2 onto Ag^0Z will be able to be statistically resolved. This work represents progress towards that aim.

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ACRONYMS

Ag^0 aerogel	Silver-functionalized aerogel
AgZ	Silver-exchanged mordenite
Ag^0Z	Reduced silver-exchanged mordenite
DOG	Dissolver off-gas
ORNL	Oak Ridge National Laboratory
TGA	Thermogravimetric analyzer

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

INITIAL EVALUATION OF EFFECTS OF NO_X ON IODINE AND METHYL IODIDE LOADING OF AgZ AND AEROGELS

1. INTRODUCTION

In a used nuclear fuel processing facility, it is known that volatile radionuclides are released at multiple steps during fuel treatment. Compliance with U.S. regulations to restrict the quantities of these radionuclides in the plant's gaseous effluent requires the capture of four radionuclides: Kr-85, C-14, H-3, and I-129. Silver-exchanged mordenite (AgZ) is being studied as a potential sorbent for I-129. Silver-functionalized aerogel (Ag^0 aerogel) is a recently developed iodine sorbent material that is also being evaluated for iodine adsorption from off-gas streams. The dissolver off-gas stream is of primary interest in this study as it is the primary release point of the iodine in aqueous reprocessing. Both elemental and organic iodine are released from the dissolver into the dissolver off-gas streams. Understanding the adsorption behavior of these species onto any proposed capture material in the presence of the other gaseous components of the dissolver off-gas (DOG) is critical to attaining the separation factors required to achieve regulatory compliance. In addition to elemental and organic forms of iodine, the DOG will also contain water vapor, NO, and NO_2 gases at an elevated temperature, as well as the other volatile radionuclides. Previous studies with NO and NO_2 on a form of AgZ that is no longer available showed measurable effects on methyl iodine loading.[1,2] It is unknown how the presence of these chemical species and potential temperature variations will affect the adsorption of iodine onto the currently available forms of AgZ and silver-functionalized silica aerogel.

To address this knowledge gap, a test matrix was designed that would statistically differentiate the effects of temperature, water vapor, NO, and NO_2 on elemental and organic iodide adsorption onto AgZ and Ag^0 aerogel. The matrix is shown in Table 1. The test matrix will be completed for each iodine species and sorbent of interest, resulting in four series of eight tests (i.e., 1: I_2/Ag^0Z, 2: CH_3I/Ag^0Z; 3: I_2/Ag^0 aerogel; 4: CH_3I/Ag^0-aerogel). The work reported here represents the completion of 25% of this test matrix for both elemental and organic (in the form of CH_3I) iodine adsorption onto AgZ, with these tests specifically evaluating the effect of NO on adsorption. These are the tests shown as Runs 1 and 4. Two subsequent FY 2015 milestones will address completion of these matrices for AgZ and Ag^0 aerogel.

Table 1. Test matrix to evaluate the effects of dissolver off-gas constituents on iodine sorption. (+ indicates high condition; - indicates low condition; highlighted lines indicate completed tests for I_2 and CH_3I adsorption onto AgZ)

Run	**Temperature** (135 or 165°C)	**NO** (0 or 1%)	**NO_2** (0 or 1%)	**Dew point** (-60 or 0°C)
1	-	-	-	-
2	+	-	-	+
3	-	+	-	+
4	+	+	-	-
5	-	-	+	-
6	+	-	+	+
7	-	+	+	+
8	+	+	+	-

2. MATERIALS AND METHODS

Thin bed loading tests were performed at ORNL in a thermogravimetric analyzer (TGA) that has the capability to produce simulated off-gas streams containing NO, NO_2, water vapor, and elemental and organic iodides to which samples may be exposed. This type of thin bed iodine loading is described by Jubin.[1] The conditions of the experiments and the effects of NO, NO_2, and water on the adsorption of either I_2 or CH_3I by reduced silver-exchanged mordenite (Ag^0Z) are presented in Table 1. The test matrix was completed twice to evaluate adsorption of both elemental and organic iodine on Ag^0Z; thus, a total of four tests were conducted, two having an elemental iodine source (in the form of a generator containing iodine crystals) and two having a methyl iodide source (in the form of a pre-mixed cylinder containing 1000 ppm CH_3I in N_2). In order to provide similar total amounts of iodine, tests with I_2 were conducted at 25 ppmv, while tests with CH_3I were conducted at 50 ppmv.

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16). It contains 11.9% silver by weight and has a pellet diameter of 1/16 in. Prior to use in this experiment, the material underwent a hydrogen reduction to reduce silver incorporated in the material. The reduction was performed by drying a deep bed of AgZ at 270°C with a low flow of argon and then reducing the material for 10 days at 270°C with a gas mixture of 4%H_2/96% N_2. Prior to exposure to the simulated off-gas stream, the Ag^0Z was allowed to equilibrate within the TGA under a dry air stream at the suggested testing temperature (either 135 or 165°C) until a stable weight was observed. The samples were then exposed to the simulated off-gas stream with compositions as shown in Table 1. Sample weight was observed to increase for several days and then reached a plateau where no further weight increase was observed. This was designated to be the maximum loading capacity of Ag^0Z under the selected conditions. The sample was then purged with dry air to remove any physisorbed iodine. Upon reaching a stable weight again, the test was concluded. The iodine loading of Ag^0Z in each test was calculated from changes in sample weight and will be confirmed by neutron activation analysis.

3. TESTING RESULTS

The results of the adsorption tests are shown in Figures 1–4. Figure 1 shows the effect of temperature and NO in the off-gas stream on the adsorption of elemental iodine onto Ag^0Z. Figure 2 shows the effect of temperature and NO on the adsorption of CH_3I onto Ag^0Z. Figure 3 compares the adsorption of elemental and organic iodine from a dry air stream onto Ag^0Z. Figure 4 compares the adsorption of elemental and organic iodine from a stream containing 1% NO onto Ag^0Z. Final iodine loadings for each test are shown in Table 2. The presence of NO reduces the capacity for iodine, presumably because it oxidizes the silver and Ag_2O does not react with iodine.

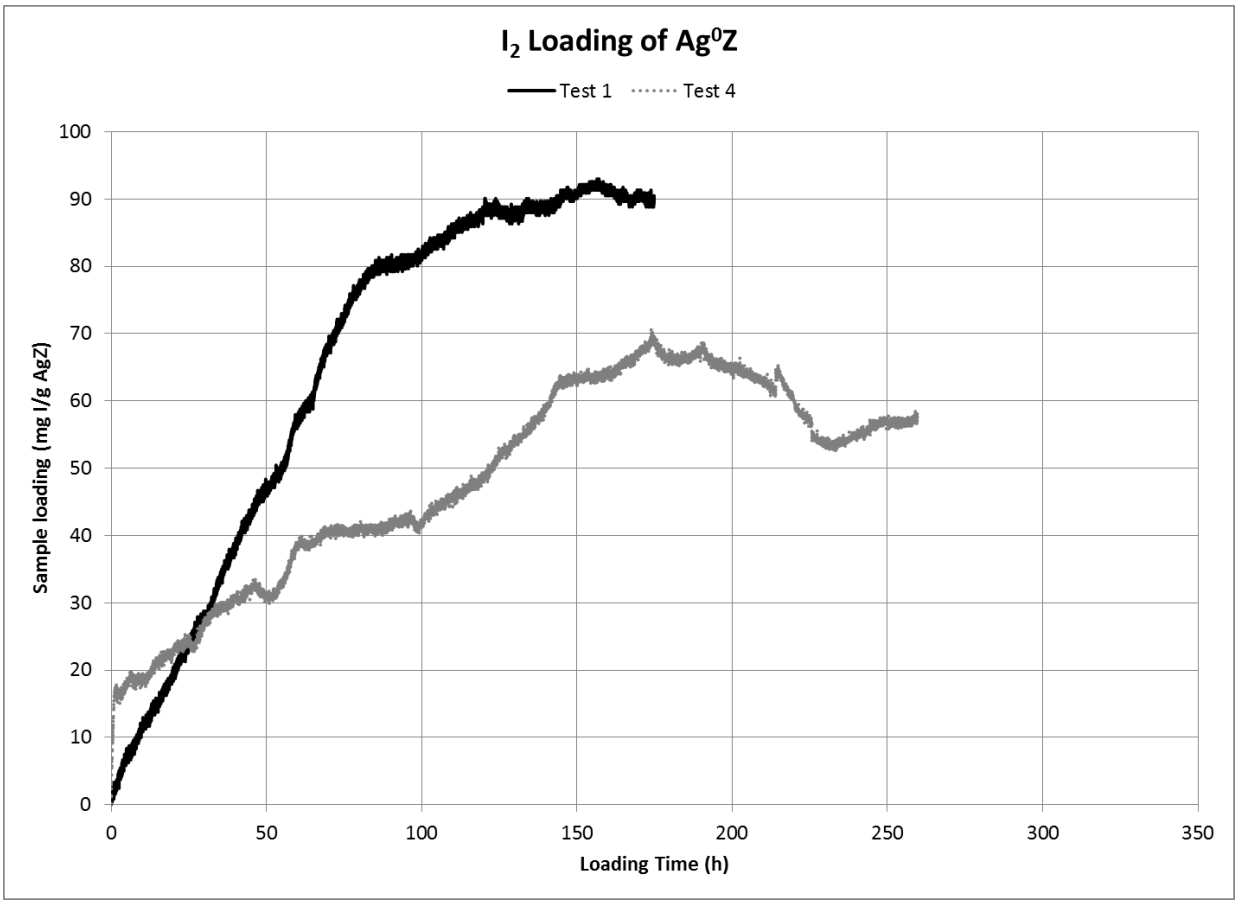

Figure 1. Adsorption of I_2 onto Ag^0Z (Test 1: 135°C, 0% NO; Test 4: 165°C, 1% NO).

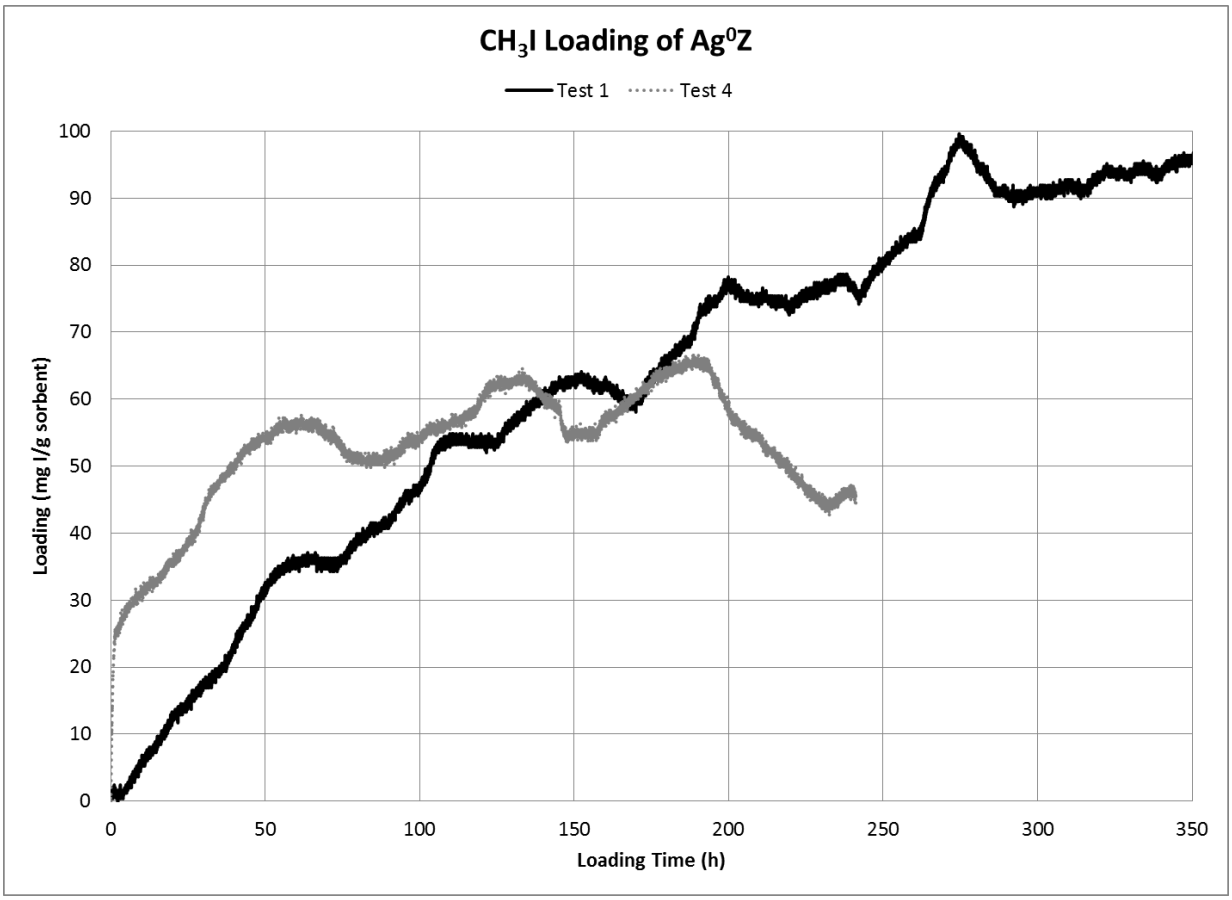

Figure 2. Adsorption of CH_3I onto Ag^0Z (Test 1: 135°C, 0% NO; Test 4: 165°C, 1% NO).

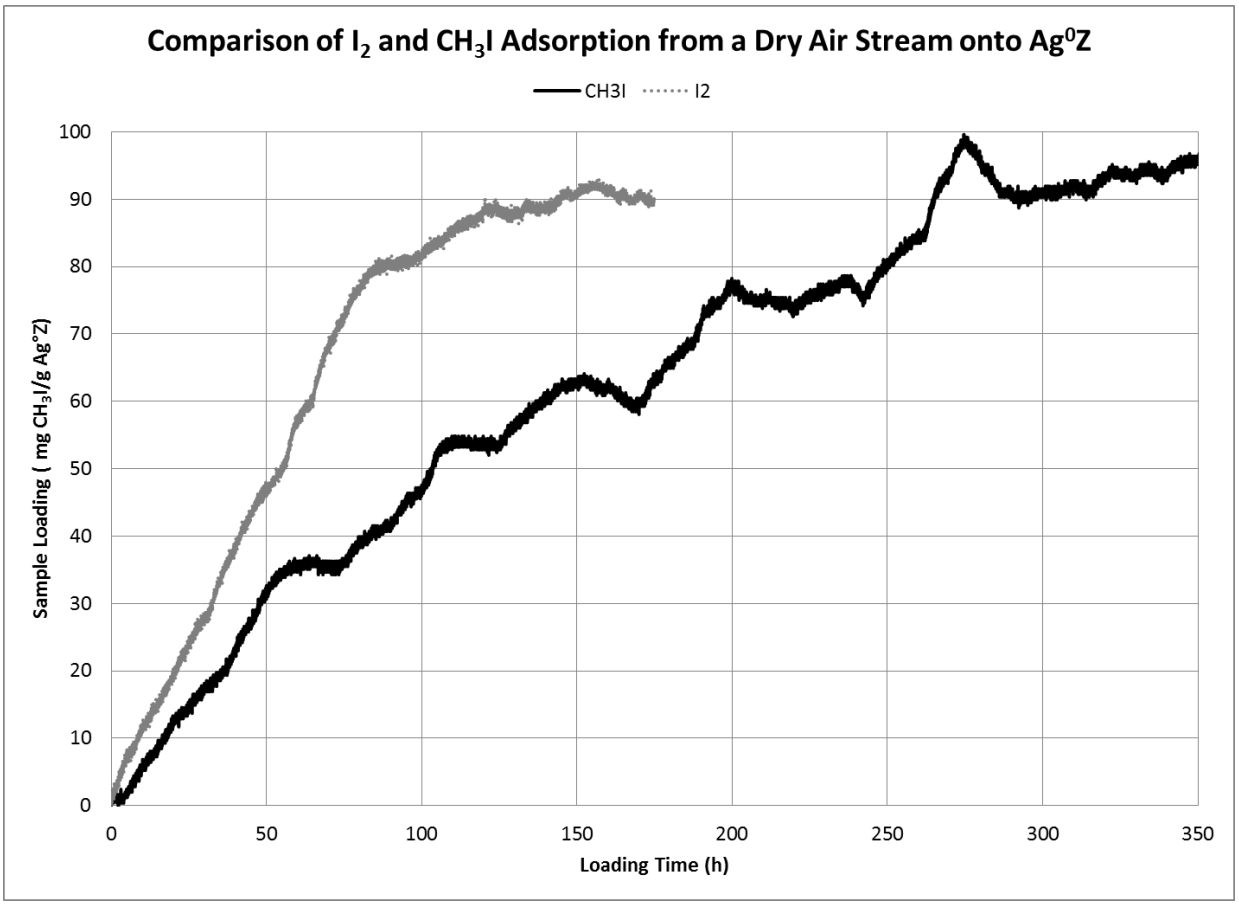

Figure 3. Adsorption of I_2 and CH_3I onto Ag^0Z ([I_2] = 25 ppm; [CH_3I] = 50 ppm; temperature 135°C).

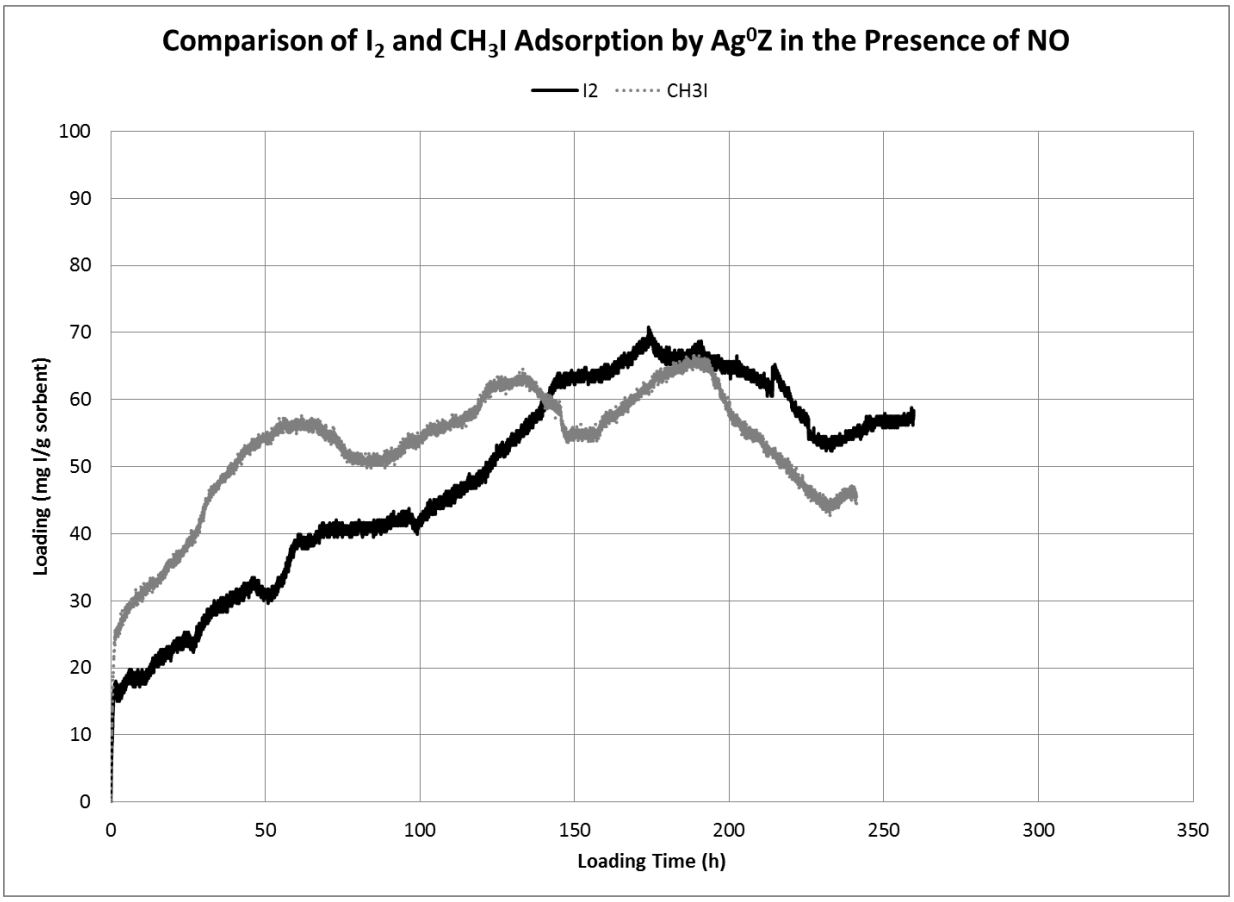

Figure 4. Adsorption of I_2 and CH_3I onto Ag^0Z in the presence of 1% NO ($[I_2]$ = 25 ppm; $[CH_3I]$ = 50 ppm; temperature 165°C).

Table 2. Iodine loading for thin bed tests.

Iodine form	[NO] (%)	Temperature (°C)	Iodine loading (mg I/g Ag^0Z)
I_2	0	135	89
I_2	1	165	55
CH_3I	0	135	93
CH_3I	1	165	45

4. DISCUSSION

Figure 1 demonstrates that the presence of 1% NO in the simulated off-gas stream decreases I_2 adsorption onto Ag^0Z by 40% (from 89 mg I/g Ag^0Z to 55 mg I/g Ag^0Z). This effect is similar for CH_3I adsorption onto Ag^0Z; Figure 2 demonstrates a 51% capacity loss (from 93 mg I/g Ag^0Z to 45 mg I/g Ag^0Z). It is unknown what effect temperature may have on the capacity of Ag^0Z for I_2 and CH_3I, but this will be resolved upon completion of the statistically designed test matrix.

When adsorbing CH_3I from a dry air stream onto Ag^0Z, the rate of sorption is approximately 50% of the I_2 adsorption rate onto Ag^0Z, despite similar total loadings. At 135°C, maximum I_2 loading occurs at 150 hours for a 2 g sample, while maximum CH_3I loading occurs at 300 hours for a similar sample size. This is shown in Figure 3.

The loading curves shown in Figure 4 confirm earlier observed behavior for the adsorption of CH_3I onto Ag^0Z in the presence of NO and NO_2.[2] In the presence of NO, the adsorption curve and final loading of CH_3I onto Ag^0Z is very similar to that of I_2. It is likely that the presence of NO in the gas stream oxidizes CH_3I to I_2 prior to adsorption, resulting in similar adsorption mechanisms for the two different species in the presence of NO. Scheele postulated the reactions for the total oxidation of CH_3I by NO (Equation 1) and calculated the free energy at similar operational temperatures to be favorable towards oxidation.[3] In the same study, partial oxidation of CH_3I was confirmed through the observation of methanol and dimethyl ether in the effluent of adsorption testing.[3]

$$7\ NO + 2\ CH_3I(g) \rightarrow I_2(g) + 2\ CO_2 + 3\ H_2O(g) + 7/2\ N_2;\ \Delta G = -1079\ kJ/mole\ (400\ K). \quad (1)$$

In conclusion, this initial evaluation provides insight into the effect of NO on the adsorption of both I_2 and CH_3I onto Ag^0Z. Although adsorption of CH_3I onto Ag^0Z occurs much more slowly than that of I_2, addition of NO to the simulated off-gas stream results in very similar loading behaviors and iodine capacities for both iodine species. This is most likely an effect of CH_3I oxidation to I_2 by NO. Completion of tests including NO_2 in the simulated off-gas stream was delayed due to vendor NO_2 production schedules. As the test matrix in Table 1 is completed for both CH_3I and I_2 sorption onto Ag^0Z, the effects of temperature, NO, NO_2, and water vapor on the sorption of CH_3I and I_2 onto Ag^0Z will be able to be statistically resolved. This work will be documented in a later FY 2015 milestone report.

5. REFERENCES

1. Jubin, R. T., *Report of the FY11 Activities of the Off-Gas Sigma Team*, Report No. FCR&D-SWF-2011-000306, U.S. Department of Energy Separations and Waste Forms Campaign, September 2011.
2. Bruffey, S. H.; Jubin, R. T., *Complete Phase 1 tests as described in the multi-lab test plan for the evaluation of CH_3I adsorption on AgZ*, Report No. FCR&D-SWF-2014-000280, U.S. Department of Energy Separations and Waste Forms Campaign, September 2014.
3. Scheele, R. D., et al., *Methyl Iodide Sorption by Reduced Silver Mordenite*, PNL-4489, UC-70, 1983.