Complete Phase I Tests As Described in the Multi-lab Test Plan for the Evaluation of CH_3I Adsorption on AgZ

Fuel Cycle Research & Development

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SUMMARY

Silver-exchanged mordenite (AgZ) has been identified as a potential sorbent for iodine present in the off-gas streams of a used nuclear fuel reprocessing facility. In such a facility, both elemental and organic forms of iodine are released from the dissolver in gaseous form. These species of iodine must be captured with high efficiency for a facility to avoid radioactive iodine release above regulatory limits in the gaseous effluent of the plant. Studies completed at Idaho National Laboratory (INL) examined the adsorption of organic iodine in the form of CH_3I by AgZ. Upon breakthrough of the feed gas through the sorbent bed, elemental iodine was observed in the effluent stream, despite the fact that the only source of iodine in the system was the CH_3I in the feed gas.[1]

This behavior does not appear to have been reported previously nor has it been independently confirmed. Thus, as a result of these prior studies, multiple knowledge gaps relating to the adsorption of CH_3I by AgZ were identified, and a multi-lab test plan, including Oak Ridge National Laboratory (ORNL), INL, Pacific Northwest National Laboratory (PNNL), and Sandia National Laboratories, was formulated to address each in a systematic way.[2] For this report, the scope of work for ORNL was further narrowed to three thin-bed experiments that would characterize CH_3I adsorption onto AgZ in the presence of water, NO, and NO_2.

Completion of these three-thin bed experiments demonstrated that organic iodine in the form of CH_3I was adsorbed by reduced silver mordenite (Ag^0Z) to a 50% higher loading than that of I_2 when adsorbed from a dry air stream. Adsorption curves suggest different adsorption mechanisms for I_2 and CH_3I. In the presence of NO and NO_2 gas, the loading of CH_3I onto Ag^0Z is suppressed and may be reversible. Further, the presence of NO and NO_2 gas appears to oxidize CH_3I to I_2; this is indicated by an adsorption curve similar to that of I_2 on Ag^0Z. Finally, the loss of organic iodine loading capacity by Ag^0Z in the presence of NO_x is unaffected by the addition of water vapor to the gas stream; no marked additional loss in capacity or retention was observed.

The adsorption capacities for CH_3I sorption onto Ag^0Z under varying conditions are shown in the table below.

Test	**Feed gas components**	**Calculated iodine loading capacity**
1	Water and NO_x	50 mg CH_3I/g Ag^0Z
2	NO_x	56 mg CH_3I/g Ag^0Z
3a	Dry	125 mg CH_3I/g Ag^0Z

Testing suggested by the test plan continues to be performed and will provide insight into the effects of temperature, gas velocity, and the concentration of CH_3I in the gas stream upon CH_3I sorption onto Ag^0Z. Upon conclusion of thin-bed testing, the information gathered by the participating laboratories will be analyzed to determine remaining knowledge gaps regarding the production of gaseous by-products of CH_3I loading on AgZ. This will allow the merit of proceeding with additional testing to be determined and will guide the proposal of specific experimental work.

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ACRONYMS

AgZ	Silver-exchanged mordenite
Ag^0Z	Reduced silver-exchanged mordenite
INL	Idaho National Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
TGA	Thermogravimetric analyzer

SEPARATIONS AND WASTE FORMS CAMPAIGN/FUEL CYCLE RESEARCH AND DEVELOPMENT: COMPLETE PHASE I TESTS AS DESCRIBED IN THE MULTI-LAB TEST PLAN FOR THE EVALUATION OF CH_3I ADSORPTION ON AgZ

1. INTRODUCTION

In a used nuclear fuel processing facility, it is known that volatile radionuclides are released at multiple steps during treatment. Compliance with U.S. regulations for the presence of these radionuclides in the plant gaseous effluent requires the capture of four: Kr-85, C-14, H-3, and I-129. Silver-exchanged mordenite (AgZ) has been identified as a potential sorbent for the I-129 released throughout the facility.

The dissolver off-gas stream is of primary interest in this study as both elemental and organic iodine are released from the dissolver in gaseous form. Understanding the adsorption behavior of these species onto any proposed capture material is critical to attaining the separation factors required to achieve regulatory compliance. To this end, in FY 2010 Idaho National Laboratory (INL) examined the adsorption of organic iodine in the form of CH_3I in dry air by AgZ. Upon breakthrough of the feed gas from the sorbent bed, elemental iodine was observed in the effluent stream. The only source of iodine in the system was the CH_3I in the feed gas.[1]

This behavior does not appear to have been reported previously nor has it been independently confirmed. Previous work at Pacific Northwest National Laboratory (PNNL), Oak Ridge National Laboratory (ORNL), and INL conducted in the late 1970s and early 1980s also focused on the adsorption of CH_3I on AgZ as this was thought to pose a greater challenge to the iodine sorption media than elemental iodine. However, these tests did not examine the effluent gas in great detail.

As a result of these prior studies, multiple knowledge gaps relating to the adsorption of CH_3I by AgZ were identified, and a multi-lab test plan (including ORNL, INL, PNNL, and Sandia National Laboratories) was formulated to address each gap in a systematic way.[2] The work proposed by Phase I of the test plan seeks to identify the gaseous by-products that arise from the adsorption of CH_3I by AgZ. Experiments suggested by Phase I are designed in detail, while subsequent phases are conceptual and will be guided by the information obtained through Phase I. The completion of all phases is needed to gain fundamental engineering data associated with the adsorption of organic iodide compounds on silver-containing sorbents.

2. THIN-BED TESTING

The objective of Phase I testing is to confirm previous observations and identify factors that may affect the adsorption behavior of CH_3I by AgZ. A series of thin-bed loading tests were suggested and then performed at ORNL in a thermogravimetric analyzer (TGA) that has the capability to produce simulated off-gas streams to which samples may be exposed. This type of thin-bed iodine loading is described by Jubin.[3] These simulated streams can be very corrosive and/or toxic, with constituents that may include elemental iodine, organic iodides, water vapor, and NO_x gases. For this report, the scope of work was further narrowed to three thin-bed experiments. Table 1 lists the selected conditions for these experiments. These conditions will allow measurement of the effects of NO, NO_2, and water on the adsorption of CH_3I by reduced silver-exchanged mordenite (Ag^0Z). The thin-bed tests suggested for completion at ORNL by the multi-lab test plan were designed to complement deep-bed testing performed at INL. The experimental results observed will be compared by the laboratories, and the effort expended by each laboratory will be efficient and without redundancy.

Table 1. Parameters selected for thin-bed testing

Test	Gas velocity (m/min)	[CH_3I] (ppm)	[NO] (ppm)	[NO_2]^a (ppm)	H_2O vapor (ppm)	Operating temperature (°C)
1	4.3	50	10,000	10,000	6000	165
2	4.3	50	10,000	10,000	<10	165
3a	4.3	50	0	0	<10	165
I_2	10	50 [I_2]	0	0	0	150

[a] Due to lack of current commercial availability of N_2O_4 gas (the precursor of NO_2), NO_2 was produced through oxidation of NO by air. Expected conversion to NO_2 is 95–98%, but the specific concentration was not determined during this testing.

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16). It contains 9.5% silver by weight and has a 1/16 in. pellet diameter. 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. The material was then reduced 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 (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 assumed to be the maximum loading capacity of Ag^0Z under the selected conditions, and 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 by sample weight and will be confirmed by neutron activation analysis in early FY 2015.

3. RESULTS

Figure 1 compares the sorption behavior of elemental iodine (I_2) on Ag^0Z at 150°C to the sorption behavior of CH_3I on Ag^0Z at 165°C (Test 3a). Both tests were conducted by exposing Ag^0Z to gas streams consisting of dry air containing iodine in the selected form (elemental or organic). However, the test with elemental iodine was conducted with a gas velocity of 10 m/min, twice the velocity of these tests. Additionally, elemental iodine is delivered with a concentration of 50 ppmv I_2, while organic iodine is delivered as 50 ppmv CH_3I, essentially half of the iodine delivered in the elemental stream. As the testing conditions for the elemental iodine test are markedly different from those used for the organic tests, only qualitative data such as total loading capacity and sorption curve shapes may be used in a comparison of the results. Elemental iodine was adsorbed by Ag^0Z at 9 wt%, while CH_3I adsorbed at 13 wt%. This corresponds to 87 mg I_2/g Ag^0Z and 125 mg CH_3I/g Ag^0Z. The markedly different shapes of the adsorption curves may be partly explained by recent publications indicating a surface-catalyzed adsorption mechanism for CH_3I onto mordenite.[4]

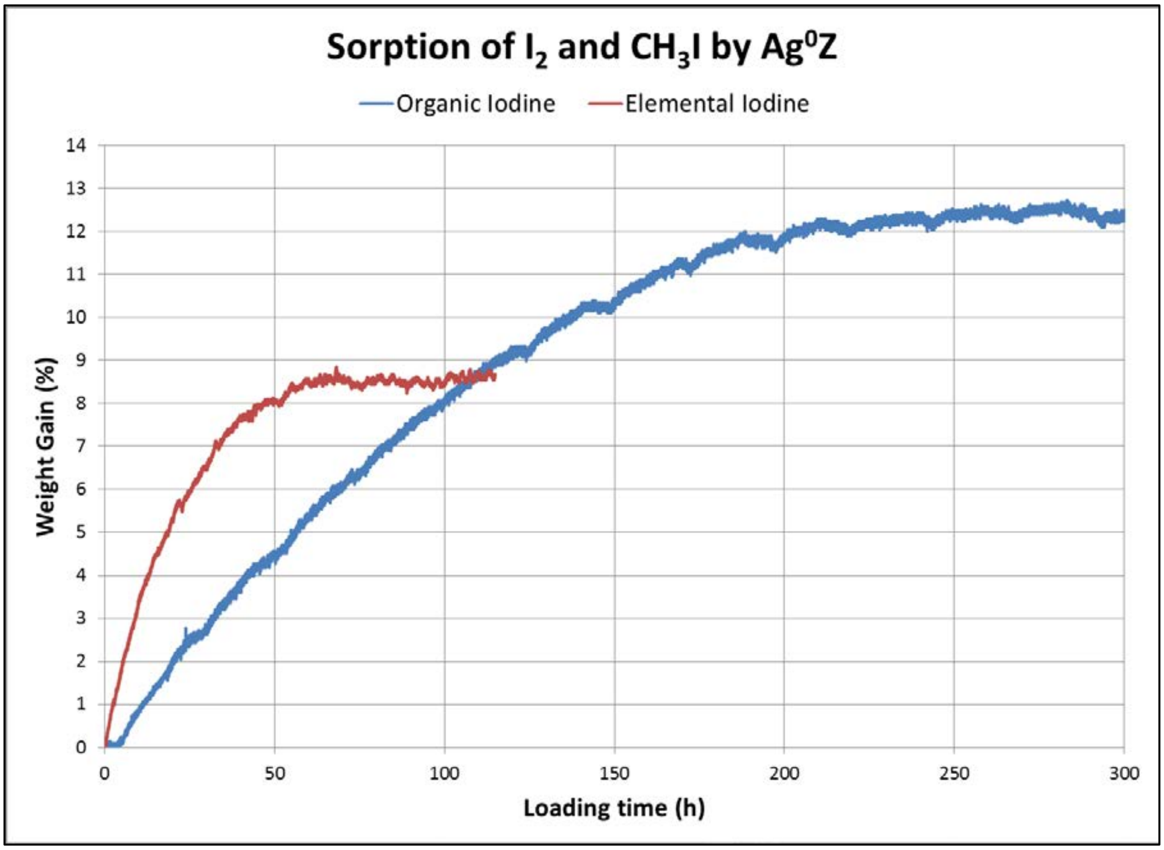

Fig. 1. Comparison of I_2 and CH_3I sorption on Ag^0Z (Test 3a).

Figure 2 compares the sorption curves obtained for Test 2 and Test 3a, as well as the same elemental iodine adsorption data plotted in Fig. 1. This provides insight into the effect of NO and NO_2 gas present in the simulated off-gas stream on the adsorption of CH_3I by Ag^0Z. In Test 2, CH_3I was adsorbed by Ag^0Z at 6 wt%, or 56 mg CH_3I/g Ag^0Z. In the presence of 10,000 ppm NO and 10,000 ppm NO_2, maximum adsorption capacity for CH_3I by Ag^0Z was lower and achieved in approximately half the time required for adsorption from a NO_x-free dry air stream. It was observed that the shape of the adsorption curve when NO_x is present is not similar to that observed in Test 3a, and the initial rate of adsorption appears to more closely mimic the adsorption behavior of I_2 onto Ag^0Z than that of CH_3I adsorption. It is possible that the presence of NO_x in the gas stream, especially the strong oxidant NO_2, may oxidize CH_3I to I_2, thus reverting back to the adsorption mechanism observed for I_2. This would support the initial observation made by INL of elemental iodine in the effluent stream of similar deep-bed testing. Scheele postulated the reactions for the total oxidation of CH_3I by both NO and NO_2 (Equations 1 and 2) and calculated the free energy at similar operational temperatures to be favorable towards oxidation.[5] 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.

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

$$7\ NO_2(g) + 4\ CH_3I(g) \rightarrow I_2(g) + 4\ CO_2 + 6\ H_2O(g) + 7/2\ N_2;\ \Delta G = -853\ \text{kJ/mole (400K)} \qquad (2)$$

A maximum weight gain of 7% occurred during Test 2, but only 6% was retained following the air purge. Chemisorption of iodine onto Ag^0Z is expected to form AgI. AgI is highly stable at these operating temperatures with a very low vapor pressure. With this in mind, if the weight loss observed during air purge includes iodine, then the portion of iodine removed may be assumed to be physisorbed, rather than chemisorbed.

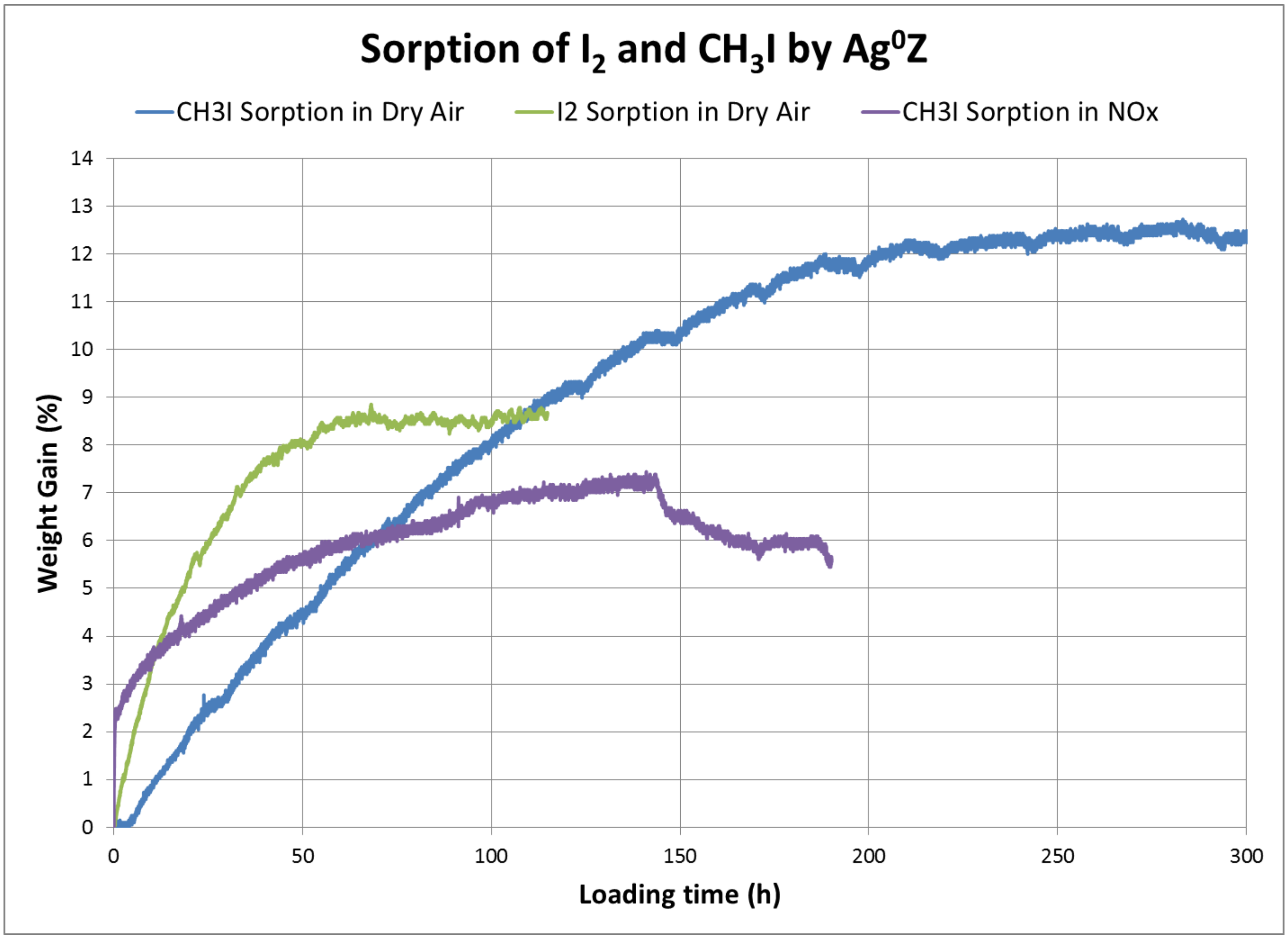

Fig. 2. Effects of NO_x on the sorption of CH_3I onto Ag^0Z (Test 2 and Test 3a).

Figure 3 compares the sorption curves obtained for all three thin-bed tests. When water was added to an NO_x-containing simulated off-gas stream, there was no added effect on loading rate for CH_3I onto Ag^0Z, and the shape of the loading curve appeared similar. The calculated loading capacities were not significantly different (50 mg CH_3I/g Ag^0Z compared to 56 mg CH_3I/g Ag^0Z). The magnitude of the weight loss observed during the air purge portion of Test 2 also appears comparable to that of Test 1. It appears that the presence of water in the simulated stream does not have an appreciable effect on either the total loading capacity or the retention of CH_3I onto Ag^0Z when NO_x is present in the gas stream.

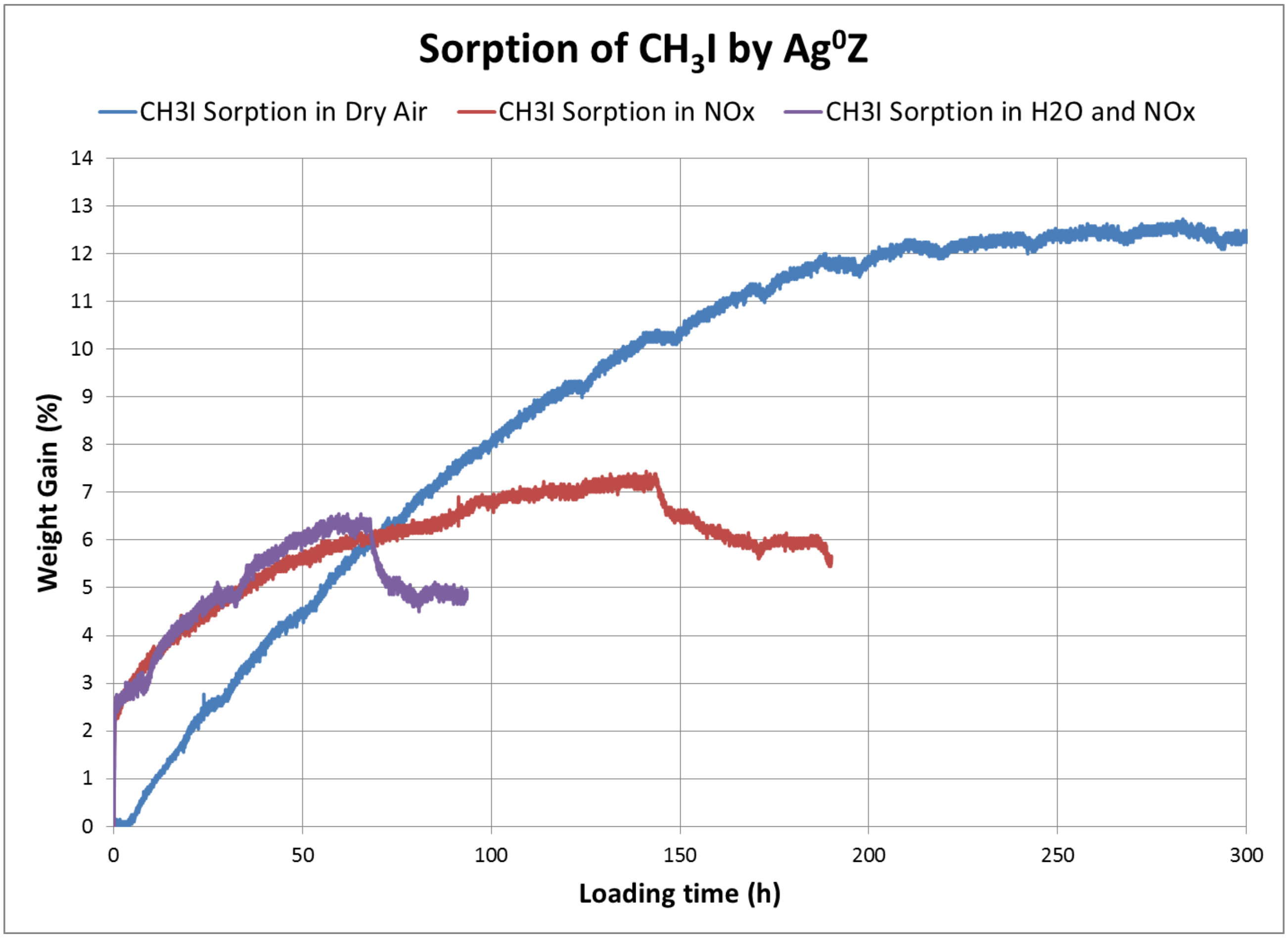

Fig. 3. Effects of water and NO_x on the sorption of CH_3I by Ag^0Z.

4. CONCLUSIONS

The observed loadings for the sorption of CH_3I onto Ag^0Z are shown in Table 2, along with the loading capacity of I_2 by Ag^0Z for comparison purposes. The CH_3I loadings will be confirmed by neutron activation analysis in FY 2015. Organic iodine in the form of CH_3I is adsorbed by Ag^0Z to a 50% higher total loading than that of I_2 when adsorbed from a dry air stream. Adsorption curves suggest different adsorption mechanisms for I_2 and CH_3I.

In the presence of NO and NO_2 gas, the loading of CH_3I onto Ag^0Z is suppressed, reaching only 40% of the loading observed from a dry air stream, and is partially reversible. Further, the presence of NO and NO_2 gas appears to oxidize CH_3I to I_2, resulting in an adsorption behavior similar to that of I_2. Finally, the loss of organic iodine loading capacity by Ag^0Z in the presence of NO_x is unaffected by the addition of water vapor to the gas stream.

Table 2. CH_3I loading capacity on Ag^0Z

Test	Feed gas components	Calculated iodine loading capacity
1	Water and NO_x	50 mg CH_3I/g Ag^0Z
2	NO_x	56 mg CH_3I/g Ag^0Z
3a	Dry	125 mg CH_3I/g Ag^0Z
I_2	Dry[a]	87 mg I_2/g Ag^0Z

[a] Conducted under different testing conditions.

The remaining thin bed tests proposed by the test plan will continue to be performed, and will provide insight into the effects of temperature, gas velocity, and the concentration of CH_3I in the gas stream upon CH_3I sorption onto Ag^0Z. Upon conclusion of Phase I thin bed testing the information gathered by the participating laboratories will be analyzed to determine remaining knowledge gaps regarding the production of gaseous by-products of CH_3I loading on AgZ. This will allow the merit of proceeding with Phase II testing to be determined and will guide the proposal of specific experimental work.

Substantial effort in the U.S. is being devoted to the design of used nuclear fuel treatment processes that are efficient and result in waste streams that are regulatory compliant. This type of fundamental research provides a scientific foundation for the process design of an off-gas treatment system, and specifically for the capture of volatile radioactive iodine from a dissolver system.

5. REFERENCES

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