Initial Evaluation of Effects of NO$_x$ on Iodine and Methyl Iodide Loading of AgZ and Aerogels

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign
S. H. Bruffey and R. T. Jubin
Oak Ridge National Laboratory
3/31/2015
FCRD-MRWFD-2015-000426
ORNL/SPR-2015/125
DOCUMENT AVAILABILITY


Website http://www.osti.gov/scitech/

Reports produced before January 1, 1996, may be purchased by members of the public from the following source:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone 703-605-6000 (1-800-553-6847)
TDD 703-487-4639
Fax 703-605-6900
E-mail info@ntis.gov
Website http://www.ntis.gov/help/ordermethods.aspx

Reports are available to DOE employees, DOE contractors, Energy Technology Data Exchange representatives, and International Nuclear Information System representatives from the following source:

Office of Scientific and Technical Information
PO Box 62
Oak Ridge, TN 37831
Telephone 865-576-8401
Fax 865-576-5728
E-mail reports@osti.gov
Website http://www.osti.gov/contact.html

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
This initial evaluation provides insight into the effect of NO on the adsorption of both I$_2$ and CH$_3$I onto reduced silver-exchanged mordenite (Ag$^0$Z). It was determined that adsorption of CH$_3$I onto Ag$^0$Z occurs at approximately 50% of the rate of I$_2$ adsorption onto Ag$^0$Z, 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$_3$I 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$_3$I and I$_2$ onto Ag$^0$Z will be able to be statistically resolved. This work represents progress towards that aim.
FIGURES

Figure 1. Adsorption of I$_2$ onto Ag$_x$Z (Test 1: 135°C, 0% NO; Test 4: 165°C, 1% NO). .........................3
Figure 2. Adsorption of CH$_3$I onto Ag$_x$Z (Test 1: 135°C, 0% NO; Test 4: 165°C, 1% NO). .....................4
Figure 3. Adsorption of I$_2$ and CH$_3$I onto Ag$_x$Z ([I$_2$] = 25 ppm; [CH$_3$I] = 50 ppm; temperature 135°C). .......................................................................................................................................... 5
Figure 4. Adsorption of I$_2$ and CH$_3$I onto Ag$_x$Z in the presence of 1% NO ([I$_2$] = 25 ppm; [CH$_3$I] = 50 ppm; temperature 165°C). ........................................................................................................................................... 6

TABLES

Table 1. Test matrix to evaluate the effects of dissolver off-gas constituents on iodine sorption. ............ 2
Table 2. Iodine loading for thin bed tests................................................................................................. 6
# ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag° aerogel</td>
<td>Silver-functionalized aerogel</td>
</tr>
<tr>
<td>AgZ</td>
<td>Silver-exchanged mordenite</td>
</tr>
<tr>
<td>Ag°Z</td>
<td>Reduced silver-exchanged mordenite</td>
</tr>
<tr>
<td>DOG</td>
<td>Dissolver off-gas</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analyzer</td>
</tr>
</tbody>
</table>
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\(^0\)Z; 2: CH\(_3\)I/Ag\(^0\)Z; 3: I\(_2\)/Ag\(^0\) aerogel; 4: CH\(_3\)I/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\(_3\)I) 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 I₂ and CH₃I adsorption onto AgZ)

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature (135 or 165°C)</th>
<th>NO (0 or 1%)</th>
<th>NO₂ (0 or 1%)</th>
<th>Dew point (-60 or 0°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>4</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>8</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

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, NO₂, 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, NO₂, and water on the adsorption of either I₂ or CH₃I by reduced silver-exchanged mordenite (Ag⁰Z) are presented in Table 1. The test matrix was completed twice to evaluate adsorption of both elemental and organic iodine on Ag⁰Z, 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 premixed cylinder containing 1000 ppm CH₃I in N₂). In order to provide similar total amounts of iodine, tests with I₂ were conducted at 25 ppmv, while tests with CH₃I 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%H₂/96% N₂. Prior to exposure to the simulated off-gas stream, the Ag⁰Z 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 Ag⁰Z 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 Ag⁰Z 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\(^0\)Z. Figure 2 shows the effect of temperature and NO on the adsorption of CH\(_3\)I onto Ag\(^0\)Z. Figure 3 compares the adsorption of elemental and organic iodine from a dry air stream onto Ag\(^0\)Z. Figure 4 compares the adsorption of elemental and organic iodine from a stream containing 1% NO onto Ag\(^0\)Z. 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\(_2\)O does not react with iodine.

![I\(_2\) Loading of Ag\(^0\)Z](image)

Figure 1. Adsorption of I\(_2\) onto Ag\(^0\)Z (Test 1: 135°C, 0% NO; Test 4: 165°C, 1% NO).
Figure 2. Adsorption of CH$_3$I onto Ag$_{0}Z$ (Test 1: 135°C, 0% NO; Test 4: 165°C, 1% NO).
Figure 3. Adsorption of I₂ and CH₃I onto Ag⁰Z ([I₂] = 25 ppm; [CH₃I] = 50 ppm; temperature 135°C).
Figure 4. Adsorption of I$_2$ and CH$_3$I onto Ag$_0$Z in the presence of 1% NO ([I$_2$] = 25 ppm; [CH$_3$I] = 50 ppm; temperature 165°C).

Table 2. Iodine loading for thin bed tests.

<table>
<thead>
<tr>
<th>Iodine form</th>
<th>[NO] (%)</th>
<th>Temperature (°C)</th>
<th>Iodine loading (mg I/g Ag$_0$Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$_2$</td>
<td>0</td>
<td>135</td>
<td>89</td>
</tr>
<tr>
<td>I$_2$</td>
<td>1</td>
<td>165</td>
<td>55</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>0</td>
<td>135</td>
<td>93</td>
</tr>
<tr>
<td>CH$_3$I</td>
<td>1</td>
<td>165</td>
<td>45</td>
</tr>
</tbody>
</table>
4. DISCUSSION

Figure 1 demonstrates that the presence of 1% NO in the simulated off-gas stream decreases I₂ adsorption onto Ag₀Z by 40% (from 89 mg I/g Ag₀Z to 55 mg I/g Ag₀Z). This effect is similar for CH₃I adsorption onto Ag₀Z; Figure 2 demonstrates a 51% capacity loss (from 93 mg I/g Ag₀Z to 45 mg I/g Ag₀Z). It is unknown what effect temperature may have on the capacity of Ag₀Z for I₂ and CH₃I, but this will be resolved upon completion of the statistically designed test matrix.

When adsorbing CH₃I from a dry air stream onto Ag₀Z, the rate of sorption is approximately 50% of the I₂ adsorption rate onto Ag₀Z, despite similar total loadings. At 135°C, maximum I₂ loading occurs at 150 hours for a 2 g sample, while maximum CH₃I 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 CH₃I onto Ag₀Z in the presence of NO and NO₂. In the presence of NO, the adsorption curve and final loading of CH₃I onto Ag₀Z is very similar to that of I₂. It is likely that the presence of NO in the gas stream oxidizes CH₃I to I₂ 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 CH₃I by NO (Equation 1) and calculated the free energy at similar operational temperatures to be favorable towards oxidation. In the same study, partial oxidation of CH₃I was confirmed through the observation of methanol and dimethyl ether in the effluent of adsorption testing.

\[
7 \text{NO} + 2 \text{CH}_3\text{I(g)} \rightarrow \text{I}_2\text{(g)} + 2 \text{CO}_2 + 3 \text{H}_2\text{O(g)} + 7/2 \text{N}_2; \Delta G = -1079 \text{kJ/mol} (400 \text{K}). \quad (1)
\]

In conclusion, this initial evaluation provides insight into the effect of NO on the adsorption of both I₂ and CH₃I onto Ag₀Z. Although adsorption of CH₃I onto Ag₀Z occurs much more slowly than that of I₂, 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 CH₃I oxidation to I₂ by NO.

Completion of tests including NO₂ in the simulated off-gas stream was delayed due to vendor NO₂ production schedules. As the test matrix in Table 1 is completed for both CH₃I and I₂ sorption onto Ag₀Z, the effects of temperature, NO, NO₂, and water vapor on the sorption of CH₃I and I₂ onto Ag₀Z will be able to be statistically resolved. This work will be documented in a later FY 2015 milestone report.

5. REFERENCES

