Iodine Capture and Mechanical Stability of Modified Silver-Functionalized Silica Aerogel

Nuclear Technology Research and Development

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

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28 June 2019
ORNL/SPR-2019/1206

SUMMARY

Silver-functionalized silica aerogel (AgAero) is a material proposed for use in the removal of iodine from the off-gas streams arising from nuclear fuel reprocessing. This material was developed by Pacific Northwest National Laboratory and has been shown to adsorb up to 300 mg of iodine per gram of AgAero. One of the challenges noted for AgAero as an iodine sorbent is its mechanical stability. Its initial particle size is >0.85 mm, but previous testing has shown that extended exposure to heated gas streams results in the degradation of the material such that the sorbent bed is compacted with a substantial amount of fines produced.

The observed mechanical degradation prompted an effort to reengineer the silica aerogel to improve the mechanical stability of the material without compromising its iodine capture characteristics. Pacific Northwest National Laboratory has modified the material with the intention of strengthening the aerogel backbone and improving mechanical durability. This reengineered material was transferred to Oak Ridge National Laboratory for extended testing to assess its mechanical durability.

Modified AgAero was continuously exposed to a CH_3I-bearing humid gas stream for 84 days. Testing was performed at 150°C with a superficial gas velocity of 10 m/min., a CH_3I concentration of 554 ppb, and an inlet dew point of 10°C. The density of the AgAero increased by 16% during testing, and the height of the column was observed to decrease by 11%. The fines produced by the material were comparable to that of previously supplied material.

Additionally, iodine loading of a thin bed of modified AgAero was performed at 150°C with a superficial gas velocity of 10 m/min. and a CH_3I concentration of 50 ppm (balance dry air) with a total test duration of 1 week. The CH_3I capture capacity of the reengineered material was 225 mg iodine per gram AgAero, as compared to a CH_3I capacity of 250 mg iodine per gram AgAero for the original material.

The primary data collected were visual observations, density measurements before and after testing, and the extent of column compaction during testing. Additionally, the material was tested to ensure that the iodine capacity of the material was not adversely impacted by the alternative methods used in the production of the reengineered material. Based on these criteria, no distinguishable improvements were observed between the material produced in fiscal years 2017 and 2019 and the mechanical stability of the aerogel in prototypic off-gas conditions remains a challenge to large-scale deployment.

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IODINE CAPTURE AND MECHANICAL STABILITY OF MODIFIED SILVER-FUNCTIONALIZED SILICA AEROGEL

1. INTRODUCTION

Silver-functionalized silica aerogel (AgAero) is a material proposed for use in the removal of iodine from the off-gas streams arising from nuclear fuel reprocessing. This material was developed by Pacific Northwest National Laboratory and has been shown to adsorb up to 300 mg of iodine per gram of AgAero with sorbent silver content of >20 wt%. Oak Ridge National Laboratory (ORNL) has characterized the iodine adsorption behavior of AgAero across a range of iodine concentrations and gas stream compositions and found the iodine adsorption performance to be comparable to a historically favored iodine sorbent, reduced silver-exchanged mordenite, when iodine adsorption is normalized to sorbent silver content. Although not yet well understood, AgAero has demonstrated that it may be more resistant to degradation from corrosive gaseous compounds found in the off-gas streams of nuclear fuel reprocessing facilities, such as NO and NO_2.

One of the challenges noted for AgAero as an iodine sorbent is its mechanical stability. Its initial particle size is >0.850 mm, but previous testing has shown that extended exposure to heated gas streams results in the degradation of the material such that the sorbent bed is compacted and a substantial amount of fines are produced. This behavior was characterized more fully in Jubin et al. (2017). In that testing, AgAero was exposed to heated (150°C) and humidified (10°C dew point) gas streams for up to 3 months. Removal of AgAero from the sorbent column by vacuum caused observable mass loss due to the loss of fines into the vacuum lines.

The observed mechanical degradation prompted an effort to reengineer the silica aerogel to improve the mechanical stability of the material without compromising its iodine capture characteristics. Pacific Northwest National Laboratory has modified the material with the intention of strengthening the aerogel backbone and improving mechanical durability. This reengineered material was transferred to ORNL for extended testing with conditions similar to those used in the prior assessment (Jubin et al. 2017). This report documents the results of the extended testing in relation to the mechanical stability of the modified AgAero and assesses the iodine capacity of the new material.

2. MATERIALS AND METHODS

Silver-functionalized silica aerogel (AgAero) was provided by Pacific Northwest National Laboratory. Details of its preparation will be provided in a report scheduled for issue later this fiscal year (FY). Before adsorption testing, the density of the as-received material was measured in quadruplicate. These measurements were made by gently pouring the material into a graduated cylinder, the base was tapped on the benchtop five times, and a volume reading was taken. The material was then poured into a weighing tray and placed on a balance for weight measurement. The post-experiment density was measured by taking the bed material that had been exposed for 12 weeks then dividing it into three segments. The density of each segment was measured individually in the same manner as the pre-exposure material, except that the material was not reweighed between each volume measurement.

A schematic of the deep-bed test system is shown in Figure 1. The sorbent was contained within a glass column with an internal diameter of 2.73 cm. A total of 23.5921 g of AgAero was poured into the glass column, corresponding to a column height of 6.35 cm. The sorbent column was contained within an oven and held at 150°C.

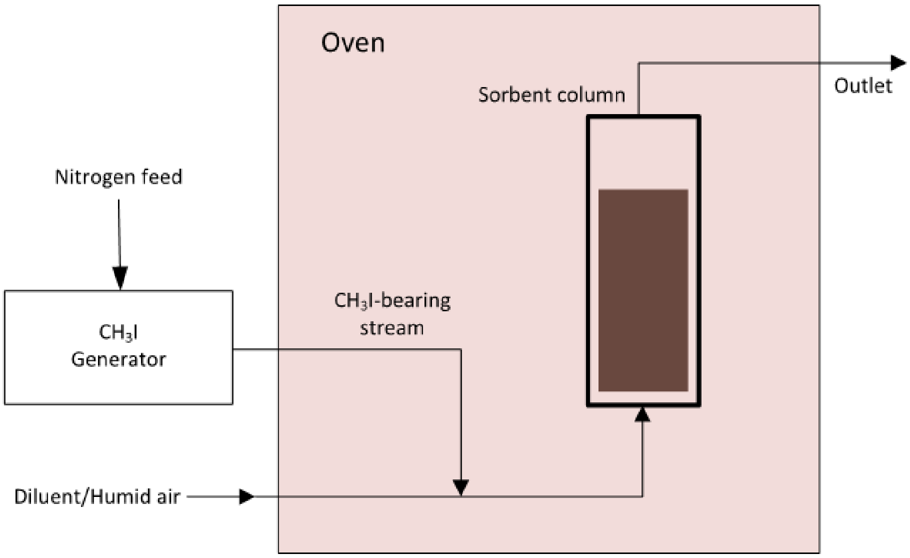

Figure 1. Schematic of test system.

A CH_3I-bearing gas stream was generated using permeation tubes provided by Kin-Tek Analytical and contained within a Kin-Tek Flexstream gas generator. Nitrogen was passed through a glass chamber containing two permeation tubes that released CH_3I at a predetermined rate at a specified temperature. This was then fed to the process and diluted with a humidified air stream. The permeation tubes used in this testing had an emission rate of ~6,000 ng/min. CH_3I at 50°C. The permeation tubes were weighed before and after testing to validate the delivery rate. Those measurements are shown in Table 1. The total gas flow rate, including the iodine-bearing stream, dilution stream, and humidified air stream, was 3.99 L/min., translating to a gas velocity of 10 m/min. at 150°C based on the cross-sectional area of the column. The concentration of CH_3I in the gas phase was calculated to be 544 ppb when using a total emission rate of 12,665 ng/min CH_3I.

Table 1. Emission rate of permeation tubes.

	Tube 1 (62103)	**Tube 2 (62098)**
Initial weight (g)	10.4741	10.6482
Final weight (g)	9.6947	9.8761
Measured emission rate (ng/min)	6362	6303

The humid air and CH_3I supply stream were piped through separate lines of tubing until they were blended before introduction into the sorbent bed. The system was visually examined for signs of corrosion before testing. All system lines were checked for leaks before testing. The assembled system is shown outside of the oven in Figure 2.

Figure 2. Assembled test system.

The test proceeded continuously for a total of 84 days online, and the setup was checked each weekday to ensure test conditions were as prescribed. Upon conclusion of the test, the AgAero bed was gently poured out and divided into three segments, and the density of each segment was measured as described previously. Removal of the sorbent from the column by pouring prevents linking bed segments to specific column depths (i.e., each segment contains portions of material from across the entire bed). The material was sent to the research reactor at University of Missouri for neutron activation analysis to determine the total amount of iodine adsorbed on the bed. Those results are pending.

The iodine capacity of the reengineered material was compared to that of the AgAero received from Pacific Northwest National Laboratory in FY 2017 using thin-bed testing. A thin bed of AgAero (~2.0 g) was contained within a custom-built thermogravimetric analyzer. This thermogravimetric analyzer is designed to weigh the sorbent continuously as it is exposed to a dry gas stream bearing analytes of interest, in this case CH_3I. Operating in this manner allows for the iodine loading of the sorbent to be observed in real-time. Once the weight gain was observed to be less than 5 mg/g for a 24 hour period, the sorbent was assumed to be saturated. It was then purged with dry air for 24 hours to remove any physisorbed CH_3I. The CH_3I concentration of the gas stream was 50 ppm, the sorbent was held at 135°C, and the superficial gas velocity (as determined using the cross-sectional area of the sorbent bed) was 10 m/min.

3. RESULTS

The 84-day AgAero column test was completed successfully. Some discoloration of the leading edge of the bed was observed, which is a likely indication of iodine loading (Figure 3).

Figure 3. AgAero column at test conclusion showing column discoloration on leading edge.

The total amount of CH_3I delivered was 1.5515 g (equivalent to 1.388 g elemental iodine). The recovered sorbent weight was 24.3049 g, an increase of 0.7128 g. Because the mass transfer zone for adsorption of CH_3I by AgAero is unknown, passage of CH_3I through the column without adsorption may account for the difference between the amount of iodine delivered to the column and the observed weight gain of the sorbent.

3.1 Density measurements

The density measurements before and after testing are shown in Table 2. The density of the material after testing was found to increase by roughly 16% over the initial material density. This increase was supported by the compaction observed in the sorbent bed during testing. The column height decreased by 0.635 cm (11%), and the bed depth was 5.7 cm at the conclusion of testing. These results were compared to testing conducted in FY 2017 using baseline AgAero material. In those tests, the measured density of the material increased 15% during testing (Jubin et al. 2017). The sorbent increased in weight by 0.77 g during testing, which may be attributable to iodine or water adsorption. This could account for a 3% increase in density.

Table 2. Density measurements of AgAero before and after testing.

Measurement	Volume (mL)	Mass (g)	Density (g/mL)
Initial-Bulk	22.8	12.9275	0.567
Initial-Bulk	23.0	12.9227	0.562
Initial-Bulk	24.2	12.8759	0.532
Initial-Bulk	24.0	12.8703	0.536
		Average	**0.549**
Final-Segment 1	7.0	4.5798	0.654
Final-Segment 1	7.0	4.5798	0.654
Final-Segment 1	7.0	4.5798	0.654
		Average	**0.654**
Final-Segment 2	9.0	6.3071	0.701
Final-Segment 2	9.5	6.3071	0.664
Final-Segment 2	9.0	6.3071	0.701
		Average	**0.688**
Final-Segment 3	22.0	13.4110	0.610
Final-Segment 3	22.0	13.4110	0.610
Final-Segment 3	21.5	13.4110	0.624
		Average	**0.614**
Average of three segments*			**0.639**

**This is a weighted average based on segment mass*

During the initial density measurements and column loading, some fines were observed, but they did not constitute a significant portion of the as-received material. The material is shown in Figure 4 along with the fines that remained in the weighing vessel. Following testing, the material did not show significant visual changes or a substantial increase in observed fines. The material removed from the column is shown in Figure 5.

Figure 4. *Left*, AgAero before use in testing. *Right*, Residual fines.

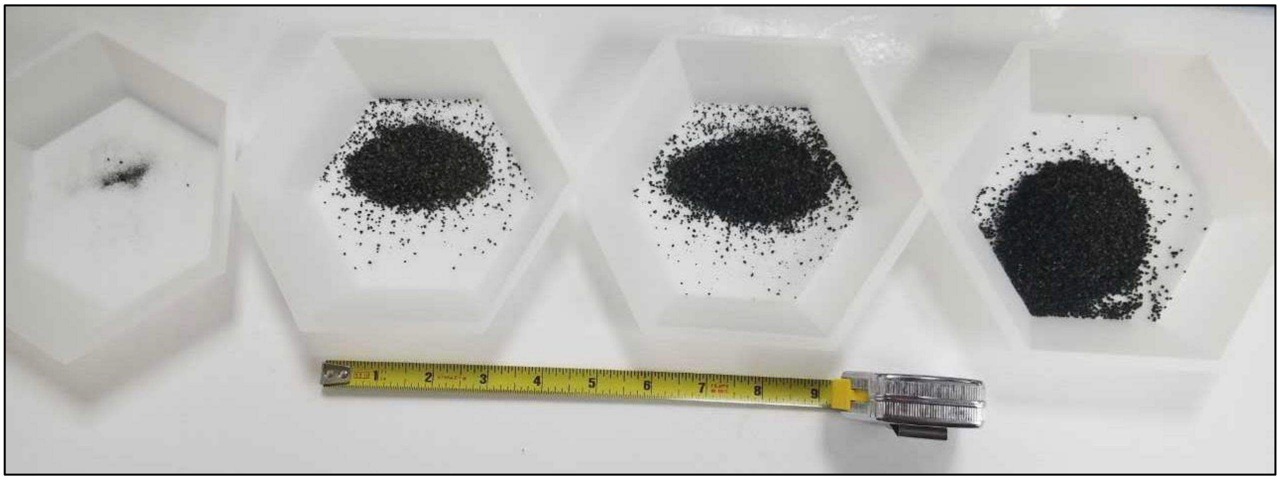

Figure 5. AgAero removed from the glass column after testing.

3.2 Iodine capacity

The methyl iodide loading curves collected during thin-bed testing in the thermogravimetric analyzer are shown in Figure 6 for FY 2017 AgAero and the reengineered FY 2019 material. These are the first loading curves collected for organic iodide on AgAero. The saturation value for the FY 2017 material was observed to be 250 mg of iodine per gram AgAero. The saturation value for FY 2019 AgAero was found to be 225 mg of iodine per gram AgAero. The rate of uptake for FY 2019 AgAero is greater than that of the FY 2017 material, but the loading curves indicate that the FY 2019 material has a decreased CH_3I capacity by an estimated 25 mg of iodine per gram of AgAero. These saturation values will be confirmed by neutron activation analysis.

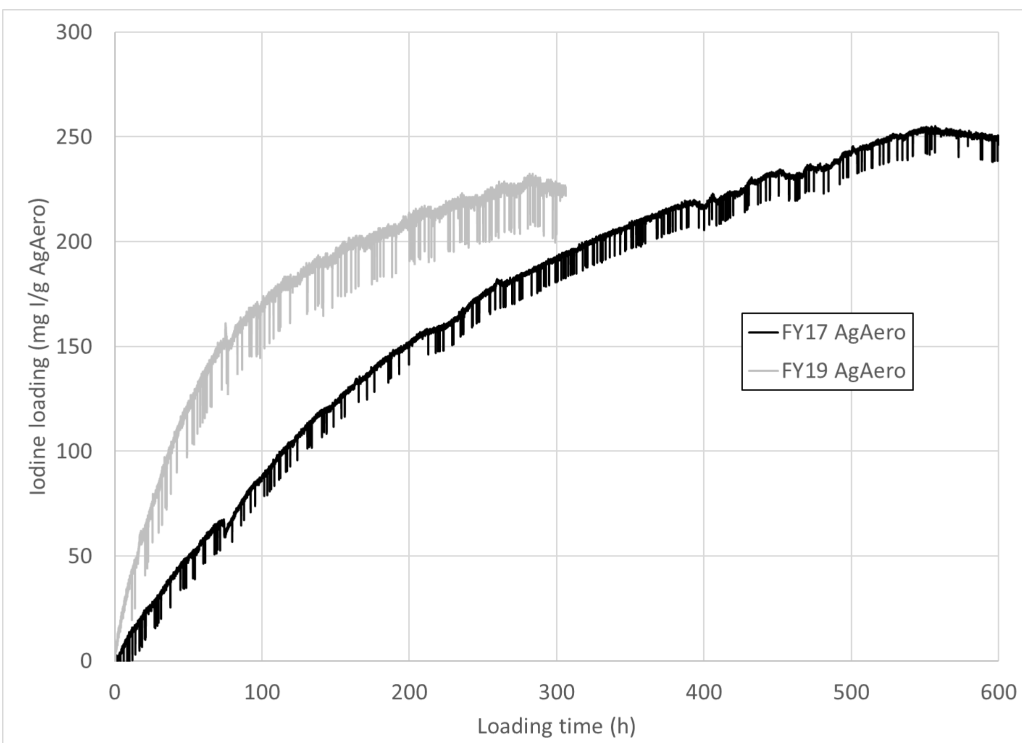

Figure 6. CH_3I loading of AgAero.

4. CONCLUSIONS

The testing described here was intended to compare the performance of baseline AgAero and the reengineered form produced in FY 2019. The primary data collected were visual observations, density measurements before and after testing, and the extent of column compaction during testing. Additionally, the material was tested to ensure that the iodine capacity of the material was not adversely impacted by the alternative methods used in the production of the reengineered material. Based on these criteria, no distinguishable improvements were observed between the material produced in FY 2017 and FY 2019, and the mechanical stability of the aerogel in prototypic off-gas conditions remains a challenge to large-scale deployment.

5. REFERENCES

Jubin, R. T., J. A. Jordan, and S. H. Bruffey. 2017. Performance of Silver-Exchanged Mordenite and Silver-functionalized Silica-Aerogel under Vessel Off-gas Conditions. Report No. ORNL/TM-2017/477. Oak Ridge National Laboratory, Oak Ridge, TN. September.