NO_2 Aging and Iodine Loading of Silver-Functionalized Aerogels

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SUMMARY

Off-gas treatment systems in used fuel reprocessing which use fixed-bed adsorbers are typically designed to operate for an extended period of time before replacement or regeneration of the adsorbent. During this time, the sorbent material will be exposed to the off-gas stream. Exposure could last for months, depending on the replacement cycle time. The gas stream will be at elevated temperature and will possibly contain a mixture of water vapor, NO_x, nitric acid vapors, and a variety of other constituents in addition to the radionuclides of capture interest. A series of studies were undertaken to evaluate the effects of long-term exposure, or aging, on proposed iodine sorbent materials under increasingly harsh off-gas conditions. Previous studies have evaluated the effects of up to 6 months of aging under dry air and under humid air conditions on the iodine loading behavior of Ag^0-functionalized aerogels. This study examines the effects of extended exposure (up to 6 months) to NO_2 on the iodine loading capacity of Ag^0-functionalized aerogels. Material aged for 1 and 2 months appeared to have a similar total loading capacity to fresh material. Over an aging period of 4 months, a loss of approximately 15% of the total iodine capacity was seen. The iodine capacity loss on silver-functionalized aerogels due to NO_2 was smaller than the iodine capacity loss due to humid or dry air aging.

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Acronyms

ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
TGA	thermogravimetric analyzer
NAA	neutron activation analysis

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SEPARATIONS AND WASTE FORMS CAMPAIGN/FUEL CYCLE RESEARCH AND DEVELOPMENT: NO_2 AGING AND IODINE LOADING OF SILVER-FUNCTIONALIZED AEROGELS

1. INTRODUCTION

In an off-gas treatment system, a capture material will typically be exposed to a gas stream for months at a time. This gas stream may be at elevated temperature and could contain water vapor, nitrogen oxides (NO_x) gas, nitric acid vapors, or a variety of other constituents making up the dissolver off-gas stream in a traditional nuclear fuel reprocessing plant. For this reason, it is important to evaluate the effects of long-term exposure, or aging, on proposed capture materials. One material under consideration is silver-functionalized (Ag^0) silica aerogel. Aerogels are being produced at Pacific Northwest National Laboratory (PNNL) and distributed to other labs for testing. Previous studies have examined the effect of extended aging, under dry or humid air conditions, on the iodine capture capacity of these aerogels. After 6 months of aging in dry air, a 22% decrease in iodine retention capacity was observed (Bruffey et al., 2012), from an initial retention capacity of 41 wt % to 33 wt %. After 6 months of aging in humid air, a 22% decrease in iodine retention capacity was seen again, this time from an initial iodine loading capacity of 33 wt% on the fresh material to 24 wt% after 6 months of humid air aging. (Bruffey et al., 2013). The aim of this study was to determine the effect of extended exposure to an air stream containing approximately 2% NO_2.

2. MATERIALS

Silver-functionalized silica aerogel was supplied by researchers at PNNL in FY 2014 for this series of tests. The material is black and granular with some light brown particles in the mixture. The minimum particle size is 850 µm. The material has a bulk density of 0.45 g/mL. It is friable and has a sandy texture. Synthesis and characterization of these materials are detailed further by Matyáš (2012). Neutron activation analysis (NAA) of the fresh material shows approximately 35 wt % silver content.

3. AGING STUDIES

Unlike the previous two studies (dry air aging and humid air aging), this series was conducted using a static 2 v/v% NO_2 gas environment. These static aging studies were similar to those reported on reduced silver mordenite (Jubin, 2013).

Stainless steel sample holders were manufactured from 6 inch sections of 316 stainless steel tubing (wall thickness 0.083 inches; internal diameter 0.834 inches). An assembled sample holder is shown in Figure 1. Valves on either end provide a means to seal the chamber after admitting gaseous reagents or after air purging.

Figure 1. Sample holder for NO_2 aging of Ag^0-functionalized aerogels.

Each sample holder was loaded with 10 grams of silver-functionalized aerogel. An aliquot of 100% NO_2 gas was charged into the holder, followed by dilution with zero air to yield a 2v/v% NO_2 environment. The sample holders were pressurized slightly above atmospheric pressure. The sample holders were then placed in an oven at 150°C for up to 4 months. At predetermined intervals, sample holders were removed from the oven. Each sample holder was allowed to cool and then purged with 1 L/min of air for at least 2 hours to remove any residual NO_x gas from the sample holder. A comparison of the samples after aging is shown in Figure 2. The samples became slightly more gray than black as aging progressed. The consistency of the material did not seem to change during aging.

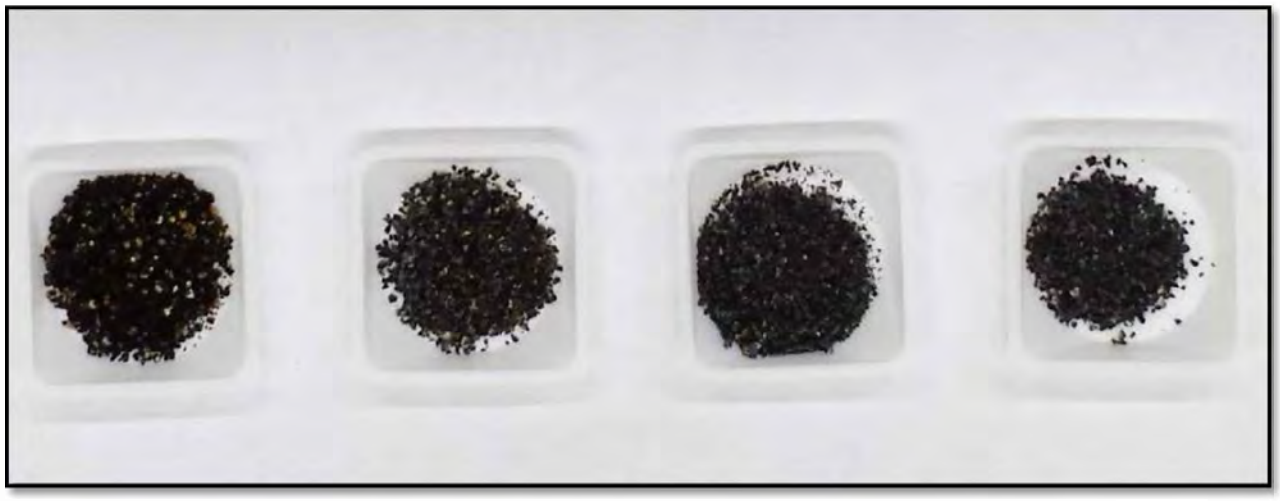

Figure 2. Aerogel, aged under NO_2 for 0, 1, 2, and 4 months (L to R).

4. IODINE LOADING STUDIES

Iodine loading of aged aerogels was conducted in a thermogravimetric analyzer (TGA). This system is described in the *Report of the FY11 Activities of the Off-Gas Sigma Team* (ORNL et al., 2011).

The aged aerogel material was loaded under conditions similar to those in previously described studies (ORNL et al., 2011). For each TGA test, the material was first dried under air for at least 24 hours. The drying air was delivered to the system at 11.85 L/min and maintained at or below a dew point of –70 °C. This drying phase ensures any possible weight loss due to water being removed from the sample has been completed before iodine loading. After drying was complete and weight was stable, the flow of iodine-containing gas was initiated at 56 ppm, maintaining a 10.3 m/min superficial velocity used in previous aerogel aging studies (Bruffey et al., 2013). This iodine loading phase of the test continued until the sample no longer appeared to be gaining mass over several hours. Once iodine loading was complete, the sample was purged with dry air containing no iodine for 24 hours, to remove any physisorbed material.

The observed weight percent changes from the TGA data for 0, 1, 2, and 4 months NO_2-aged Ag°-functionalized aerogel samples are shown in Figure 3. The data shown begin at the time the iodine stream was introduced to the sample and end after the 24 hour purging period. Final observed weight gains for each sample are shown in Table 1. The iodine loadings as determined from the TGA loading curves were confirmed by NAA.

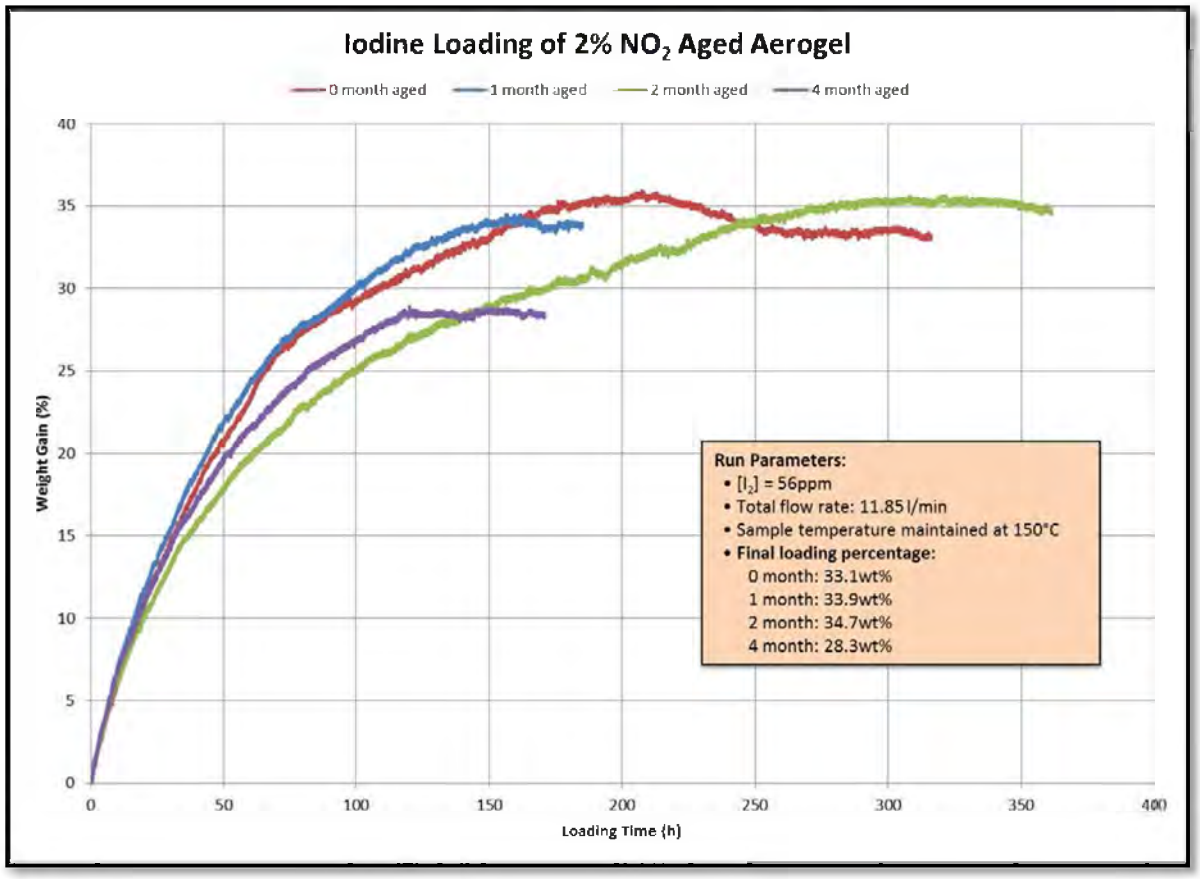

Figure 3. Iodine loading curves for NO_2-aged aerogels.

5. RESULTS

The aging and loading studies on the silver-functionalized aerogel were conducted successfully. Aging the aerogel material under static conditions with dry air containing 2% NO_2 resulted in an approximately 15% loss in iodine capacity with extended exposure. Very limited loss in iodine capacity was observed in the first 2 months of NO_2 exposure. The loss of capacity in this static test was less pronounced than in the flowing moist air series of aging tests in which a 22% loss in capacity was observed after as little as 1 month of aging.

Data from the TGA tests are compared with data from NAA in Table 1. For the unaged or 0 month case, the NAA iodine loading is within 0.4 wt % of the TGA value, which is outside the uncertainty range. For the 1 month case, the NAA value is 3 wt % below the reported TGA value; the TGA value indicated no loss in iodine capacity after 1 month of aging, but comparison of the 0 and 1 month NAA values shows approximately a 10% loss in capacity. The data for TGA and NAA again show similar values for the material iodine loading capacity in the sample aged for 2 months, which appears to have a higher iodine loading capacity than the material aged for 0 months. The 2 month sample had a much slower loading rate and was exposed to the iodine stream for a much longer period. Data for the material aged for 4 months show a higher initial rate of loading, but total loading was reached more quickly. Additional possible sources of variability in iodine loading are the variations in the aerogel material and variation in the NO_x concentrations in the sample. The static aging tests introduce variability to aging comparisons that is not the same as in a flowing air stream aging study. During the flowing studies, a constant stream composition was maintained. In the static aging studies, the changes in the composition of the gas streams in each individual sample holder are not known over time. The initial concentration in the sample holders is the only measure of the NO_2 composition. Once the sample holders were heated, NO_2 gas may oxidize silver in the aerogel, introducing an NO byproduct into the cylinder. The NO can react with available oxygen in the system to create more NO_2. Therefore, throughout the aging time of the sealed holders, there are unmeasured changes in the concentrations of NO, NO_2, and oxygen.

Table 1. Iodine content of NO_2-aged aerogels

Aging time (months)	TGA weight gain (%)	NAA I_2 (%)	Uncertainty NAA I_2 (%)
0	33.1	33.5	0.0904
1	33.9	30.9	0.0773
2	34.7	34.3	0.158
4	28.3	23.2	0.107

6. CONCLUSIONS

The aging and loading studies on the silver-functionalized aerogel were conducted successfully. Smaller losses in capacity were seen in the aerogel iodine loading capacity due to NO_2 exposure than to humid air exposure.

It was observed that the material provided in this study has a lower overall iodine loading capacity, even before aging, than the material provided for dry aging studies. This material had a similar initial iodine capacity to the materials used in the humid air aging studies.

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