Preparation of NO_2-Aged Silver-Functionalized Silica-Aerogel and Silver Mordenite Samples

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J. A. Jordan
S. H. Bruffey

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SUMMARY

Reprocessing used nuclear fuel can result in the volatilization of radioactive gaseous species, including ^{129}I, into the various process off-gas streams. In order to comply with US regulatory requirements, plant off-gas streams must be treated to remove the iodine prior to discharging the off-gas into the environment. The performance of available gas removal methods depends not only on the concentration of the volatile radioisotope of interest, but also on other constituents that could be present in the reprocessing off-gas streams. Some of the constituents, such as NO_x produced during fuel dissolution, are known to have deleterious effects on the capture performance of silver-based sorbents used for iodine removal.

Commercially available reduced silver mordenite (AgZ) has an iodine saturation concentration of 7.0–9.0 wt%, and its iodine sorption capacity is reduced by 20–50% as a result of NO_2 aging. Silver-functionalized silica aerogel (AgAerogel), an alternative for iodine capture, has an initial iodine saturation of 29.0 wt% and its iodine capacity is only reduced by 15% from NO_2 aging. Understanding the differences in aging behavior between AgZ and AgAerogel is critical to determining the behavior of these sorbents under realistic off-gas conditions. To assist in future technical studies on this topic, samples of both AgZ and AgAerogel were aged with NO_2. In the experiment, 10.2190 g of AgZ and 10.1771 g of AgAerogel were exposed to a static 0.75% NO_2/dry air blend for a period of 28 days. The samples were then removed and stored under argon until needed for future experiments.

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CONTENTS

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LIST OF FIGURES

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ACRONYMS

AgAerogel	silver-functionalized aerogel
AgZ	silver-exchanged mordenite
Ag^0Z	reduced silver-exchanged mordenite
BET	Brunauer–Emmett–Teller
EPA	US Environmental Protection Agency
LPM	liters per minute
NEUP	Nuclear Energy University Program
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
SEM	scanning electron microscopy
UNF	used nuclear fuel
XRD	x-ray diffraction

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PREPARATION OF NO_2-AGED AGAEROGEL AND AGZ SAMPLES

1. INTRODUCTION

Reprocessing used nuclear fuel (UNF) can result in the volatilization of several radioactive gaseous species, including ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I, into the various process off-gas streams. These off-gas streams require treatment prior to environmental discharge in order to comply with US Environmental Protection Agency (EPA) regulations on the emissions of volatile radioisotopes to the environment. Several silver-based solid sorbent materials are being evaluated for potential use in the treatment of off-gas streams containing iodine (Jubin et al. 2012). The performance of these materials depends not only on the concentrations of the volatile radioisotope of interest, but also on any other gas constituents that could be present in the off-gas streams. Some of the constituents have been shown to adversely impact the capacity of the sorbent materials (Bruffey et al. 2015a; Bruffey et al. 2015b).

It is important to understand the effects of these various constituents in gas capture performance. As oxidizing gases, NO and NO_2 have been shown to have deleterious effects on the iodine capture performance of silver-exchanged mordenite (AgZ) (Bruffey et al., 2015b; Jubin et al. 2013). Commercially available reduced AgZ has an iodine saturation concentration of 7.0–9.0 wt% AgZ, and aging in a static 2% NO_2 environment for 1–2 months can reduce AgZ's loading capacity by 25–50% (Jubin, et al. 2013). Silver-functionalized silica-aerogel (AgAerogel) has an iodine saturation concentration of 29.0 wt%, but 2 months of static 2% NO_2 aging was shown to only reduce the loading capacity by 15% (Bruffey et al. 2015a). The origin of the difference in the performance degradation between these two materials is not currently understood.

The objective of this effort is to prepare samples of NO_x aged AgZ and Ag aerogel that can be utilized at this and other laboratories to aid in gaining insight into the aging mechanism(s).

2. MATERIALS AND METHODS

Commercially available silver-exchanged mordenite (AgZ, Ionex-Type Ag 900 E16) was procured from Molecular Products in an engineered pelletized form that contains 9.5 wt% silver. The binder for the engineered form is a proprietary clay-based material that is added to the crystalline zeolite structure. The silver in this material was reduced through extended exposure at elevated temperature to a H_2/N_2 gas blend. Reduced AgAerogel was provided by PNNL in FY 2014. The AgAerogel had a bulk density of 614 kg/m^3 (as measured by ORNL), a surface area of 134 m^2/g, a pore volume of 0.46 x 10^{-6} m^3/g, an adsorption pore size of 17 nm, and a desorption pore size of 13 nm (Matyas 2013). Testing of the AgAerogel demonstrated an initial unaged iodine loading capacity of 29.0 wt% (Bruffey et al. 2015a).

The aging tubes used in this experiment (Figure 1) were assembled from 1 in. (outer diameter) 316 stainless steel tubing with a wall thickness of 0.083 in., resulting in a cross section of 0.546 in.^{2} (3.52 cm^2). The overall volume of a single loading chamber was measured to be approximately 90 cm^3.

Figure 1. Aging tube.

Tube 1 contained 10.2190 g of AgZ and Tube 2 contained 10.1771 g of AgAerogel. For each experiment, the sorbents were contained between metal mesh that allowed gas flow through the chamber but did not allow for sorbent movement. A 0.75% NO_2/bal dry air gas blend (inlet dew point of −70 °C) was passed through the loaded aging tubes for 2.5 minutes each to replace the ambient air environment of the chamber with the NO_2 gas blend; this resulted in approximately 65 volume changes (air turnover within the tube). The tubes were then sealed with the NO_2 gas blend inside and held at 150 °C for 28 days. The chambers were then allowed to cool and then purged with dry air for a period of 2.25 hours at 2 liters per minute (LPM). The aged materials were stored in glass sample vials under argon gas.

3. RESULTS

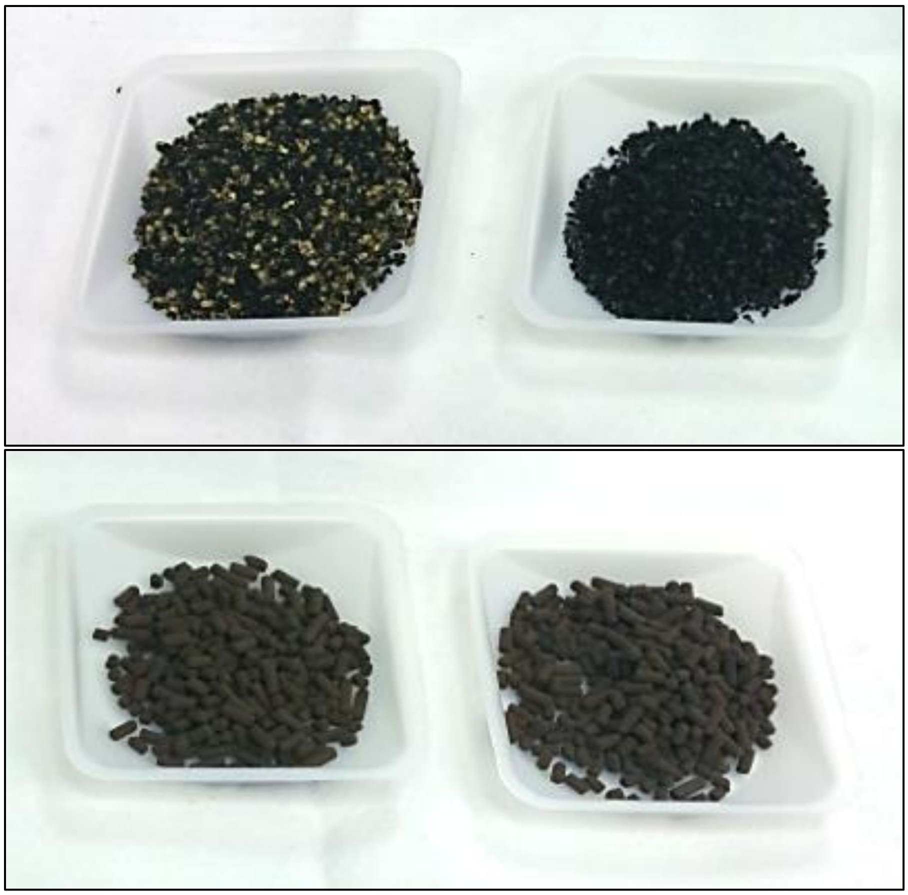

Figure 2. Top, left-to-right: unaged AgAerogel and aged AgAerogel; Bottom, left-to-right: unaged Ag^0Z and aged Ag^0Z.

The AgAerogel sample underwent observable physical changes upon exposure to the NO_2 stream. AgAerogel (the two top images in Figure 2) experienced a color change in some of the material, losing the yellow flecks of color in the original material. The AgZ was visually unchanged through the aging process.

4. DISCUSSION AND CONCLUSIONS

Samples of two silver-based iodine sorbents, AgAerogel and AgZ, were exposed to NO_2 for approximately 1 month in order to allow future testing of these sorbents (and these samples in particular) for the effect of NO_2 aging on iodine capture. The AgAerogel sample underwent a color change in the presence of NO_2, while the AgZ remained visually similar to unaged AgZ. The iodine loading capacity of both samples will be determined to confirm that these materials exhibit similar degradation in capacity as previously observed. Once these loading tests have been completed, samples of these materials will be available for use at other laboratories upon request. Subsequent evaluations are expected to include surface and structure analysis via scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET), and x-ray diffraction (XRD) characterization. The samples were prepared at ORNL and will be analyzed by collaborators at Pacific Northwest National Laboratory (PNNL) and various Nuclear Energy University Programs (NEUPs).

5. REFERENCES

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