Iodine Loading of NO Aged Silver Exchanged Mordenite

Fuel Cycle Research & Development

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SUMMARY

In an off-gas treatment system for used nuclear fuel processing, a solid sorbent 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, gaseous nitrogen oxides (NO_x), nitric acid vapors, and a variety of other constituents. For this reason, it is important to evaluate the effects of long-term exposure, or aging, on proposed sorbents. Silver exchanged mordenite (AgZ) is being studied at Oak Ridge National Laboratory (ORNL) to determine its iodine sorption capacity after long term exposure to increasingly more complex chemical environments. Studies previously conducted at ORNL investigated the effects of aging reduced silver exchanged mordenite (Ag^0Z) in dry air, moist air, and NO_2. This study investigated the effects of extended exposure to nitric oxide (NO) gas on the iodine capture performance of Ag^0Z. A deep bed of Ag^0Z was aged in a 1% nitric oxide (NO) air stream, and portions of the bed were removed at pre-determined intervals. After being removed from the NO stream, each sample was loaded with iodine in a thin bed configuration. These samples were analyzed by neutron activation analysis (NAA) to quantify the iodine content in the sample.

Samples were removed at one week and one month. A 78% decrease in sample capacity was seen after one week of exposure, with no further decrease observed after 1 month of aging. The observed loss in capacity is larger in magnitude than previous studies exposing Ag^0Z to dry air, moist air, or NO_2 gas. The aging study was terminated after one month and repeated; this successfully demonstrated the reproducibility of the results.

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FIGURES

TABLE

ACRONYMS

AgZ	Silver mordenite
Ag^0Z	Reduced silver mordenite
NAA	Neutron activation analysis
NO	Nitric oxide
NO_2	nitrogen dioxide
NO_x	Nitrogen oxides
ORNL	Oak Ridge National Laboratory

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IODINE LOADING OF NO AGED SILVER EXCHANGED MORDENITE

1. INTRODUCTION

In an off-gas treatment system for used nuclear fuel processing, a solid sorbent 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, gaseous nitrogen oxides (NO_x), nitric acid vapors, and a variety of other constituents. For this reason, it is important to evaluate the effects of long-term exposure, or aging, on proposed sorbents. Silver exchanged mordenite (AgZ) is being studied at Oak Ridge National Laboratory (ORNL) to determine its iodine sorption capacity after long term exposure to increasingly more complex chemical environments.

Studies previously conducted at ORNL investigated the effects of aging reduced silver exchanged mordenite (Ag^0Z) in dry air and in moist air. These studies reported approximately a 40% loss in capacity after six months of dry air aging and after one month of humid air aging (Jubin, 2011). The work described in this report investigated the effects of extended exposure to NO gas on the iodine capture capacity of Ag^0Z. This will provide insight into the behavior of Ag^0Z when exposed to the air stream around the dissolver in a fuel reprocessing plant, which may contain low concentrations of NO_x gases ranging from 1-3% (Birdwell, 1991). Studies have been performed on long-term static aging of Ag^0Z in a static NO_2 environment (Bruffey, 2013). The study described here is an aging study in a flowing air stream of 1% NO, which is expected to more closely mimic actual process conditions and provide a basis for more direct comparison to the previous dry and moist air studies.

2. MATERIALS AND METHODS

2.1 Reduced silver mordenite (Ag^0Z)

Silver mordenite was obtained from Molecular Products in an engineered form (Ionex-Type Ag 900 E16). It contains 9.5% silver by weight and has a 1/16 inch pellet diameter. The silver present in the mordenite was reduced with hydrogen for ten days at 270°C with a gas mixture of 4%H_2/96% N_2, as described in previous reports (Jubin, 2012.)

2.2 Aging Study

The sorbent was aged by exposing the sample to a dry air stream containing 1% NO. The superficial velocity of the gas stream was 3.5 m/min. Sample temperature was maintained at 150°C using a tube furnace, seen in Figure 1. It is estimated that approximately 10% of the NO converts to NO_2 as the NO stream mixes with the air stream in the experimental apparatus and across the sample bed.

Samples were removed at 1 week and 1 month. The aging was terminated after one month. The experiment was repeated to demonstrate the reproducibility of the results, and the duplicate 1 week NO-aged sample behaved as seen previously.

Figure 1. Aging Tube Furnace.

2.3 Iodine loading of Ag^0Z

The samples of Ag^0Z were loaded with iodine in a thermo-gravimetric analyzer (TGA). This type of thin bed iodine loading is described by Jubin (2011). The superficial velocity of the gas stream was 10 m/min, and the iodine concentration was 50 ppm. Prior to loading with iodine, the material was dried in the column with a dry air stream at 150°C. The samples were loaded with iodine until there was no apparent increase in weight, and were then purged with dry air only for 24 hours to remove any physisorbed iodine. The iodine loading of each sample was determined by neutron activation analysis (NAA).

3. RESULTS

The iodine loading curves for the 1 week and 1 month samples are shown in Figure 2, along with the iodine loading curve for the unaged Ag^0Z. A decrease of 78% in iodine loading capacity is seen in both the one week and one month aged sample. The original capacity of the reduced silver mordenite was 9 wt%; upon the conclusion of aging it was observed to be 2 wt %. This loss in capacity was much larger than was seen with static NO_2 aging studies (Bruffey et al., 2013) and the dry and moist aging. The data for these tests are shown in Figure 2. For verification, an additional 1 week aging study was conducted. The data from the verification test are shown in Figure 3.

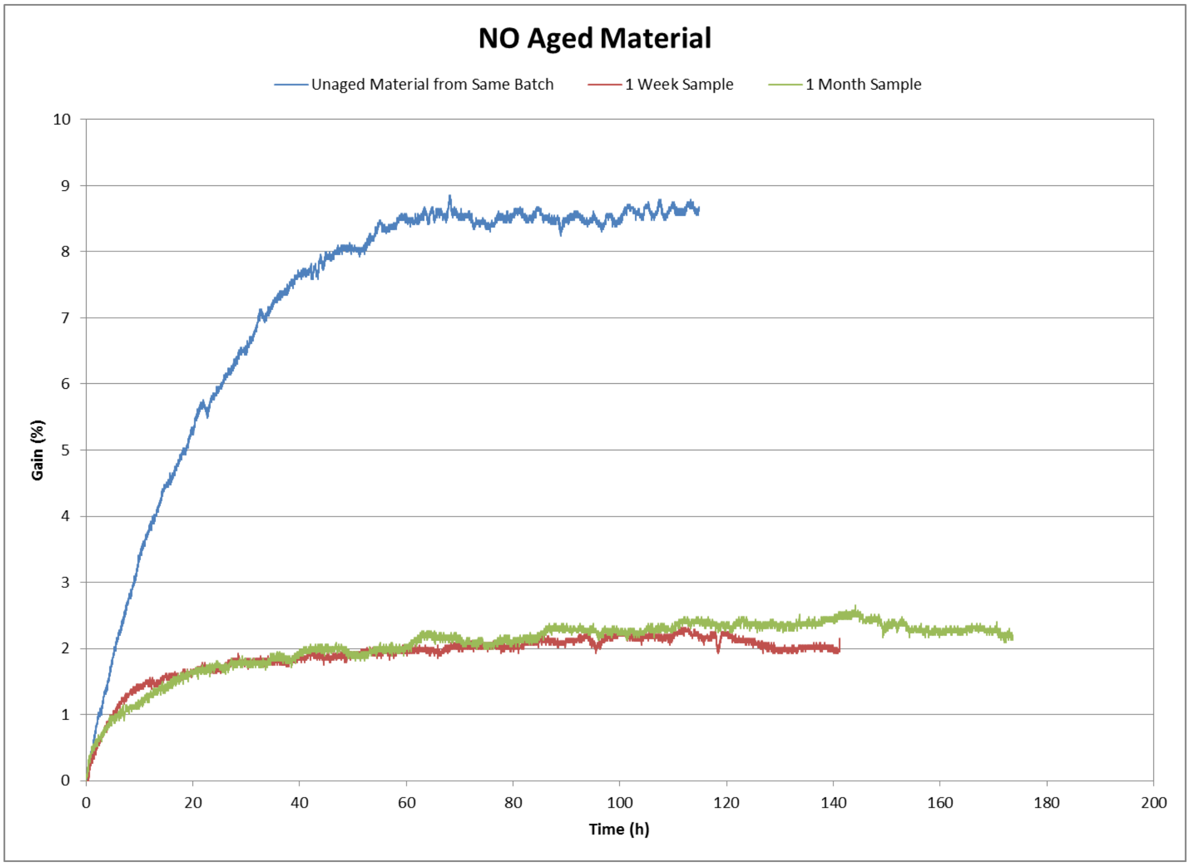

Figure 2. TGA Data for First Aging Study.

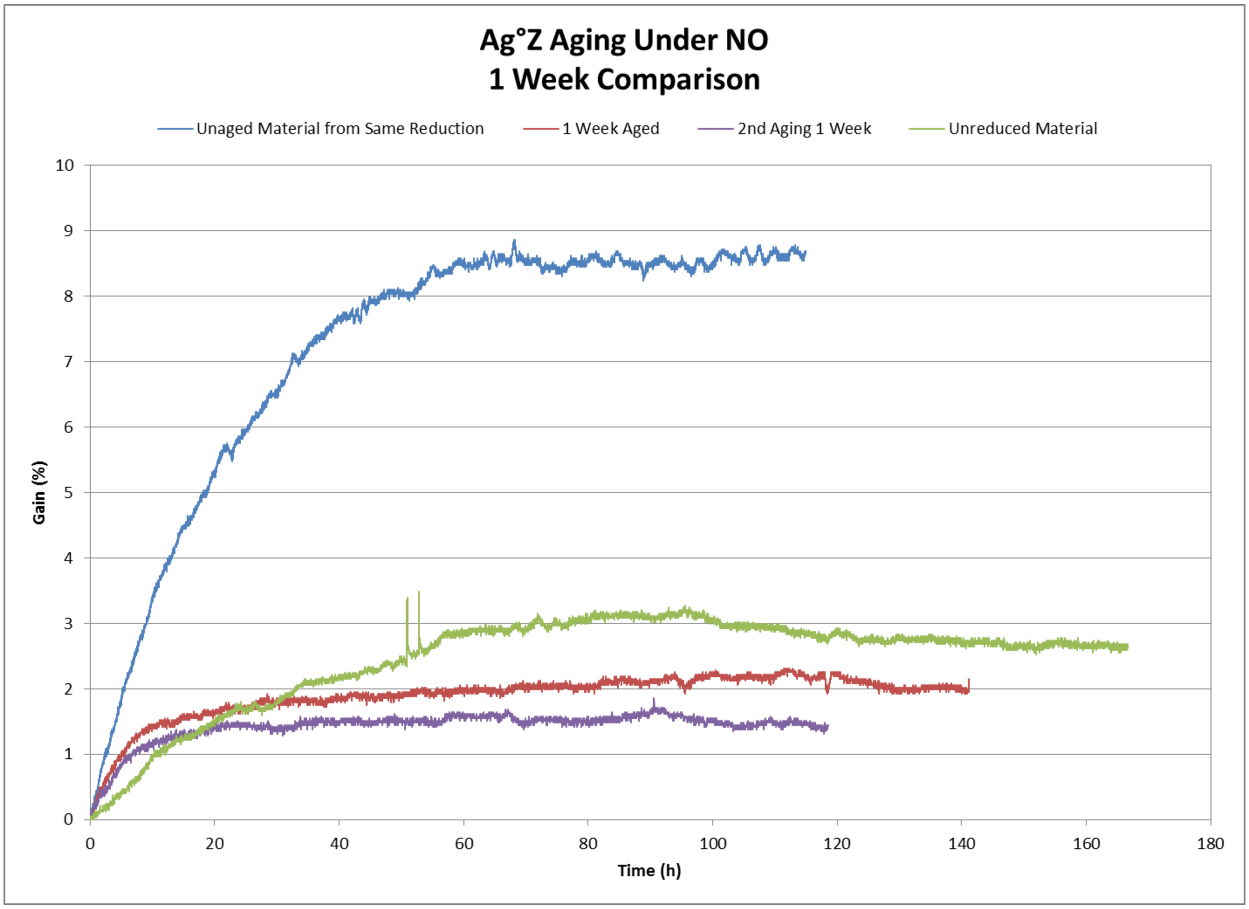

Figure 3. TGA Data for 1 Week Comparison.

The data from the TGA are reported as a percent increase in weight. The initial weight for the TGA samples is taken as the mordenite sample's weight after it has been dried for 24 hours. The drying removes any residual moisture that may have been introduced into the sample during handling. Then, the percent weight gain is taken as the iodine loading of the sample.

Neutron activation analysis results for the first aging study are shown in Table 1. The iodine content listed from NAA is as a percent of the total mass of the sample that was sent for analysis.

Table 1. NAA Results for First Aging Study.

Aging Time	I_2 Content (wt %)	Uncertainty (wt %)
0	7.19	0.260
1 Week	3.427	0.010
1 Month	2.849	0.009

The decrease in sample capacity is greater than the losses seen in the dry air study (Jubin, 2011). The combination of the NO, NO_2, and oxygen (from the diluent air stream) appear to oxidize the silver in the sample and possibly cause other changes in the mordenite. Oxidizing the silver alone would lower the material capacity to the unreduced state. The aged material has less capacity than the unreduced material.

4. CONCLUSIONS

A decrease of 78% in iodine capture capacity was observed in NO-aged Ag^0Z, occurring in the first week of exposure to 1% NO. Exposure to 1% NO and air while maintaining sample temperature at 150 °C appears to cause the silver mordenite material to lose the majority of its iodine capture capacity. The capacity loss appears to be greater than oxidation of the silver in the sample alone, indicating a possible change in the sorbent.

5. REFERENCE

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