Complete NO and NO_2 Aging Study for AgZ

Fuel Cycle Research & Development

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DISCLAIMER

SUMMARY

In an off-gas system within a nuclear fuel reprocessing plant, any capture material will be exposed to a gas stream for months at a time. This gas stream may be at elevated temperature and could contain water, NO_x gas, or a variety of other constituents that comprise the off-gas stream. For this reason, it is important to understand the effects of long-term exposure, or aging, on proposed capture materials. One material under consideration is silver-exchanged mordenite (AgZ). The aim of this study was to determine the effect of extended exposure at 150°C to an air stream containing NO on the iodine capture capacity of the hydrogen reduced form of AgZ designated as Ag^0Z. The study was originally also intended to expand on the static NO_2 aging studies by exposing Ag^0Z to a flowing stream of NO_2 for an extended period of time, but those tests were delayed due to NO_2 production schedules by the gas vendor.

Unreduced silver mordenite has a loading capacity of approximately 25 mg I/g AgZ and that capacity is increased to 100 mg I/g Ag^0Z upon reduction. It appears that extended exposure of AgZ to 1% NO at 150°C may not only neutralize the increased capacity gained by reduction, but perhaps degrade the sorbent even further. Loss of 80% of sorbent capacity and surface area was observed after 8 weeks of exposure to a 1% NO stream at 150°C.

Investigations continue into the effects of aging by off-gas components on iodine sorbents. Future work will age silver mordenite with streams containing NO_2. As the simulated off-gas streams become more complex and more corrosive, the ability of AgZ to withstand conditions present in off-gas streams will be more fully known.

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ACRONYMS

AgZ	Silver exchanged mordenite
Ag^0Z	Reduced silver exchanged mordenite
BET	Brunauer-Emmett-Teller method

MATERIALS RECOVERY AND WASTE FORM DEVELOPMENT CAMPAIGN

COMPLETE NO AND NO_2 AGING STUDY FOR AgZ

1. INTRODUCTION

In an off-gas system within a nuclear fuel reprocessing plant, any capture material will be exposed to a gas stream for months at a time. This gas stream may be at elevated temperature and could contain water, NO_x gas, or a variety of other constituents that comprise the off-gas stream. For this reason, it is important to understand the effects of long-term exposure, or aging, on proposed capture materials. One material under consideration is silver-exchanged mordenite (AgZ). AgZ is a commercially produced material containing natural mordenite that has been converted to an engineered form by combination with a clay binder and then subjected to ion exchange to incorporate silver into the mordenite structure. The hydrogen reduced form of this material is designated Ag^0Z. Previous studies have examined the effect of extended aging at 150°C under a dry air streams, a humid air stream, and a static NO_2 environment on the iodine capture capacity of Ag^0Z.[1,2] The loss in iodine capacity due to aging in each environment is shown in Table 1. The aim of this study was to determine the effect of extended exposure at 150°C to an air stream containing NO on the iodine capture capacity of Ag^0Z. The study was originally also intended to expand on the static NO_2 aging studies by exposing Ag^0Z to a flowing stream of NO_2 for an extended period of time, but those tests were delayed due to NO_2 production schedules beyond our control. The results of this aging study in concert with other previously completed studies will provide insight into the ability of Ag^0Z to withstand exposure to corrosive off-gas streams.

Table 1: Effects of aging environment on the iodine capacity of Ag^0Z

Aging Environment	Aging Time (months)	Capacity loss (%)
Flowing dry air; 150°C	6	40
Flowing humid air; 150°C	4	60
Static 2% NO_2; 150°C	2	30

2. MATERIALS AND METHODS

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16) (Figure 1). It contains 11.9% silver by weight and has 1/16 inch pellet diameter. Prior to use in this experiment, the material underwent a hydrogen reduction at 230°C to increase the total iodine loading capacity. Details of this procedure can be found in Anderson, 2012.[3] After reduction, the Ag^0Z material was loaded with iodine in a thermo-gravimetric analyzer and determined to have an iodine loading capacity of 9.7%. This type of testing is described in Jubin, 2011.[2]

Figure 1: Engineered silver mordenite supplied by Molecular Products

The aging study was conducted in a deep bed test system, shown in Figure 2. A 34 g charge of Ag^0Z was contained in a stainless steel tube (I.D. 1.87 in.) located in a tube furnace. The furnace was held at 150°C for the duration of the study. A dry air stream (dew point < 70°C) was mixed with 100% NO in ¼ inch stainless steel tubing approximately 12 inches prior to entering the tube furnace. There was a second gap of approximately 12 inches between the bottom of the tube furnace and the sample bed; this was to ensure that the gas was fully heated prior to encountering Ag^0Z and that the sample charge was fully located in the heating zone of the furnace. Thermocouples were placed in this heating zone, in the sample bed, and at the tube exit to monitor the gas and sample temperatures. The gas velocity through the tube was 3.5 m/min.

At selected intervals of 1, 4, and 8 weeks the flow was suspended and the oven cooled. The material was removed from the tube and gently mixed to ensure homogeneity, then a 10-15 g sample was removed and the remainder of the material was returned to the tube and the test was continued. After the aging test was complete the 4 and 8 week samples were loaded with iodine in a thermo-gravimetric analyzer as referenced above. The final iodine loading for each sample was determined by neutron activation analysis.

Surface area determination was performed by the Brunauer-Emmett-Teller (BET) method at Idaho National Laboratory. Prior to BET analysis the samples were degassed at 250°C for 4 hours.

3. TESTING RESULTS

Iodine loading curves for 0, 4, and 8 week aged samples are shown in Figure 2 and the total iodine capacity for each is shown in Table 1. A loss of over 70% iodine capacity is observed with only 4 weeks of aging, and after 8 weeks of aging the total capacity loss increases to 85%. Surface areas of the aged samples (Table 2) also show a significant decrease.

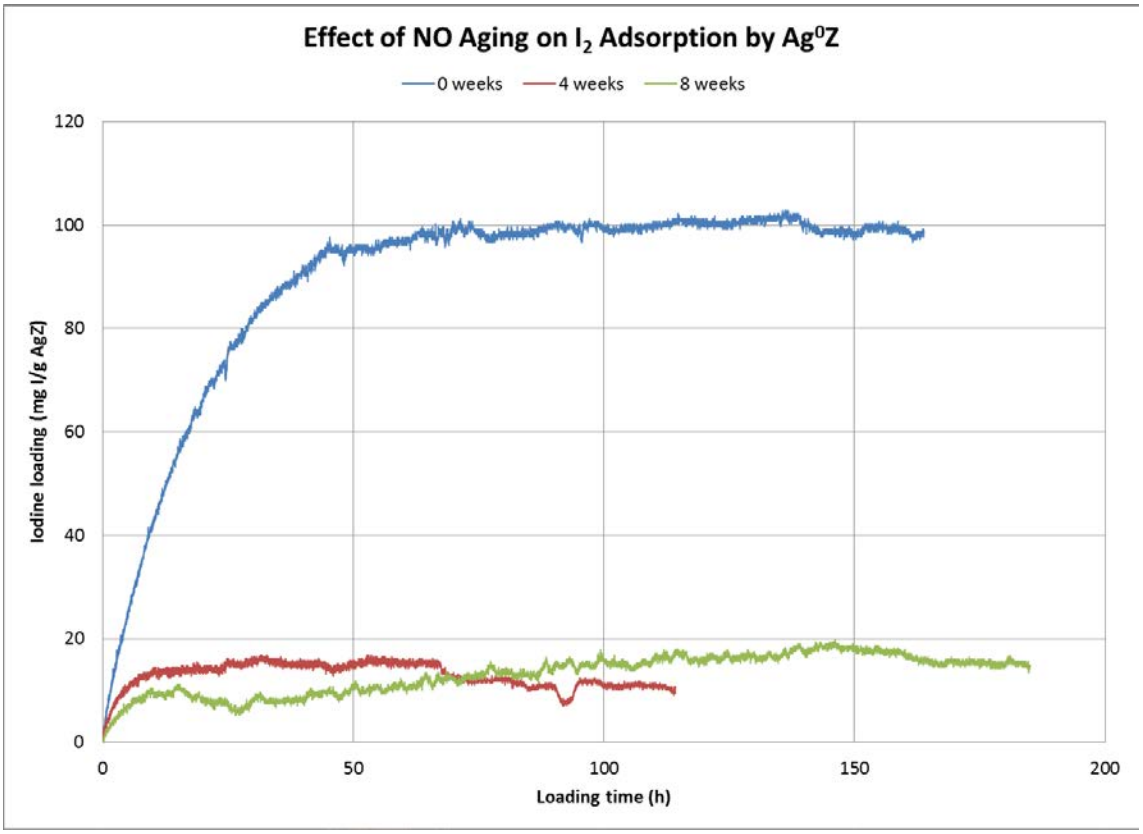

Figure 2: Effect of NO aging on I_2 adsorption by Ag^0Z

Table 2: Iodine loading capacities for NO-aged Ag^0Z

Aging Time (weeks)	Iodine Loading Capacity (mg I/g Ag^0Z)
0	97
4	27
8	15

Table 3: BET surface area analysis for NO-aged Ag^0Z

Aging Time (weeks)	Surface area (mg^2/g)	P/P_0
0	128	0.06-0.11
1	16	0.05-0.10
4	21	0.05-0.07
8	24	0.05-0.23

4. DISCUSSION

Unreduced silver mordenite has a loading capacity of approximately 25 mg I/g AgZ and that capacity is increased to ~100 mg I/g Ag^0Z upon reduction, as observed for the 0 week (un-aged) sample. The TGA data suggests that extended exposure to 1% NO at 150°C may not only neutralize the increased capacity gained by reduction, but perhaps degrade the sorbent even further. Loss of 80% of sorbent capacity and surface area was observed after 8 weeks of exposure to a 1% NO stream at 150°C.

Characterization of these samples is ongoing and will include analysis by X-ray diffraction and scanning electron microscopy. It is expected that these analyses will provide insight into fundamental changes in the material that may contribute to loss of iodine loading capacity. For example, oxidation of reduced silver to silver oxide forms may be a primary cause of capacity loss and will be investigated through X-ray diffraction.

Investigations continue into the effects of aging by off-gas components on iodine sorbents. An alternate sorbent, silver functionalized aerogel, has been subjected to aging with 1% NO and iodine loading tests will be performed to determine any potential iodine capacity loss. AgZ and silver functionalized aerogel will both be aged under streams containing NO_2. As the simulated off-gas streams become more complex and more corrosive, the ability of both AgZ and silver-functionalized aerogel to withstand conditions present in off-gas streams will be more fully known.

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5. REFERENCES

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