Aging of Iodine-Loaded Silver Mordenite in NO_2

Fuel Cycle Research & Development

Prepared for
U.S. Department of Energy
Fuel Cycle Research and Development
S.H. Bruffey
R.T. Jubin
K.K. Anderson
J.F. Walker, Jr.
Oak Ridge National Laboratory

April 30, 2014
FCRD-SWF-2014-000465
ORNL/LTR-2014/153

SUMMARY

Used nuclear fuel facilities need to control and minimize radioactive emissions. Off-gas systems are designed to remove radioactive contaminants, such as ^{85}Kr, ^{14}C, ^{3}H, and ^{129}I. In an off-gas system, 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 comprising the dissolver off-gas stream in a 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 reduced silver mordenite (Ag^0Z), which is recognized for its efficient iodine capture properties. Iodine is immobilized on Ag^0Z as AgI, a solid with low volatility (m.p. ≥ 500°C). The aim of this study was to determine whether extended aging at elevated temperature in a nominally 2% NO_2 environment would result in a loss of immobilized iodine from this material due to either physical or chemical changes that might occur during aging. Charges of iodine-loaded reduced silver mordenite (I_2-Ag^0Z) were exposed to a 2% NO_2 environment for 1, 2, 3, and 4 months at 150°C, then analyzed for iodine losses

The aging study was completed successfully. The material did not visibly change color or form. The results demonstrate that no significant iodine loss was observed over the course of 4 months of 2% NO_2 aging of I_2-Ag^0Z at elevated temperature within the margin of error and the variability (~10%) in the loading along the beds. This provides assurance that iodine will remain immobilized on Ag^0Z during extended online use in an off-gas capture treatment system. Future tests should expose I_2-Ag^0Z to progressively more complex feed gases in an effort to accurately replicate the conditions expected in a reprocessing facility.

CONTENTS

FIGURES

TABLE

ACRONYMS

AgZ	Silver mordenite
Ag^0Z	Reduced silver mordenite
I_2-Ag^0Z	Iodine-loaded reduced silver mordenite

This page intentionally left blank

SEPARATIONS AND WASTE FORMS CAMPAIGN/FUEL CYCLE RESEARCH AND DEVELOPMENT:

AGING OF IODINE-LOADED SILVER MORDENITE IN NO_2

1. INTRODUCTION

Used nuclear fuel facilities need to control and minimize radioactive emissions. Off-gas systems are designed to remove radioactive contaminants, such as ^{85}Kr, ^{14}C, ^{3}H, and ^{129}I. In an off-gas system, 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 comprising the dissolver off-gas stream in a 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 reduced silver mordenite (Ag^0Z), which is recognized for its efficient iodine capture properties. Iodine is immobilized on Ag^0Z as AgI, a solid with low volatility (m. p. $\geq$ 500°C). The aim of this study was to determine whether extended aging at elevated temperature in a nominally 2% NO_2 environment would result in a loss of immobilized iodine from this material due to either physical or chemical changes that might occur during aging. Charges of iodine-loaded reduced silver mordenite (I_2-Ag^0Z) were exposed to a 2% NO_2 environment for 1, 2, 3, and 4 months at 150°C, and then analyzed for iodine losses. The results of this study will provide insight into the behavior of Ag^0Z when used as an iodine capture material in an off-gas treatment facility. Specifically, as Ag^0Z ages in a feed stream containing NO_2 while simultaneously capturing iodine from that same feed stream, the effects of NO_2 exposure on iodine retention become clear.

2. MATERIALS AND METHODS

2.1 Reduced silver mordenite (Ag^0Z)

Silver mordenite was obtained from Molecular Products in an engineered pelletized form (Ionex-Type Ag 900 E16). It contains 9.5% silver by weight and has a 1/16 inch pellet diameter. Prior to use in this experiment, the material underwent a hydrogen reduction to reduce silver incorporated in the material. The reduction was performed by drying a deep bed of AgZ at 270°C with a low flow of argon and then reducing the material for 10 days at 270°C with a gas mixture of 4%H_2/96% N_2. The resultant Ag^0Z was then loaded with iodine in a thermo-gravimetric analyzer and determined to have an iodine loading capacity of 7.2 wt%. This type of thin bed iodine loading is described by Jubin (2011).

2.2 Iodine loading of Ag^0Z

An 84 g batch of Ag^0Z was loaded with iodine in a deep bed test system. This system is shown in Figure 1. A dry (dew point ≈ -70°C) iodine-bearing air stream was contacted with the deep bed of Ag^0Z. The Ag^0Z was contained in a stainless steel column (diameter 2.66 cm) inside an oven held at 150°C. 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 to ensure no residual moisture was present. The material was then loaded with iodine for 3 days, at which point iodine was seen in the effluent stream and it was assumed that breakthrough had occurred. The column was then purged with a dry air stream for 3 days to remove physisorbed iodine. After 3 days no iodine was observed in the effluent stream, and it was assumed that all physisorbed iodine had been removed. The

I_2-Ag^0Z was then analyzed for iodine by neutron activation analysis and determined to contain 7.2 wt % iodine. This corresponds directly with the loading capacity observed in the thermo-gravimetric testing.

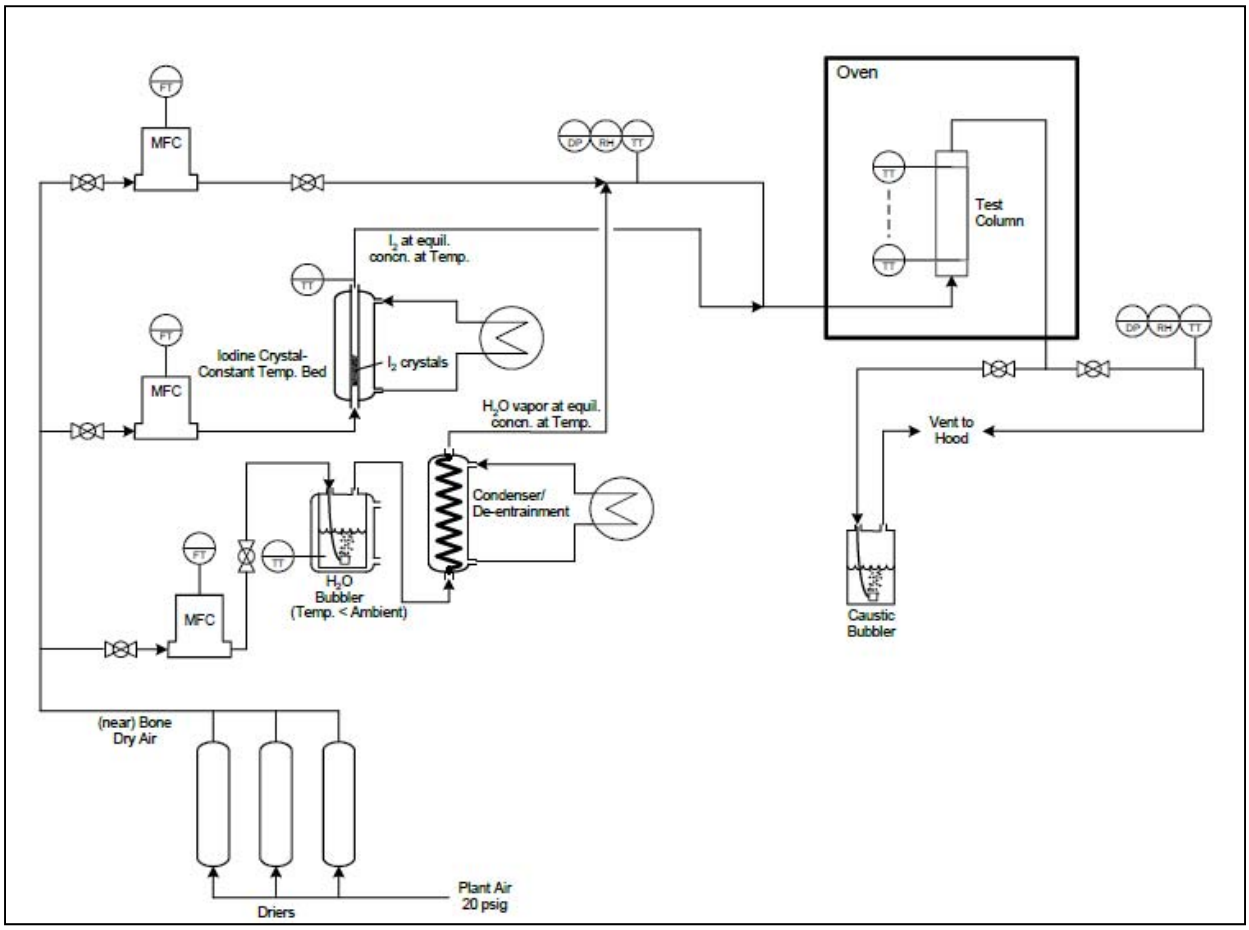

Figure 1: Schematic diagram of deep bed iodine loading system

3. AGING STUDY

Four stainless steel sample holders were manufactured from 6 inch sections of 316 stainless steel tubing (wall thickness 0.083 inch; internal diameter 0.834 inch). An assembled sample holder is shown in Figure 2. Valves on either end allowed gas flow through the chamber during air purging.

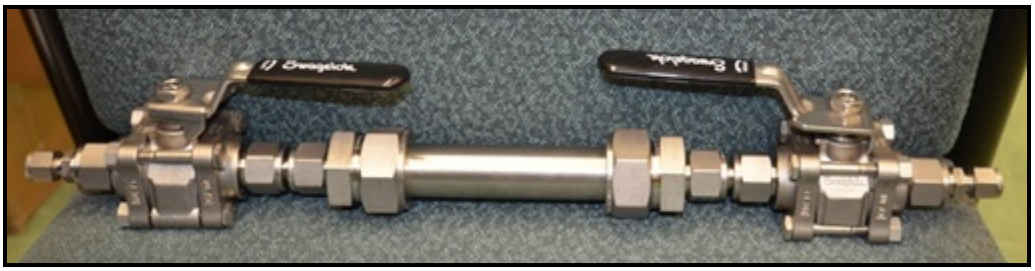

Figure 2: Sample holder for NO_2 aging of I_2-Ag^0Z

Ten grams of Ag^0Z was placed in each sample holder. To create a nominally 2% NO_2 environment, each tube was first evacuated using a vacuum pump. An aliquot of N_2O_4 gas was delivered into the tube, followed by dilution with zero air to yield 2% NO_2. N_2O_4 is present as a liquid/gas mixture at room temperature, and at this temperature the vapor phase consists of roughly 70% N_2O_4 and 30% NO_2 (disassociated N_2O_4). The sample holders were pressurized slightly above atmosphere with this mixture of N_2O_4/NO_2/zero air. After the holders were charged they were placed in a 150°C oven for the duration of the aging study. Heating of the samples will change the gas composition present in the tubes. At 150°C, 100% of the N_2O_4 has decomposed to NO_2. Therefore, the true concentration of NO_2 during the aging study may have approached 3%.

The aging study proceeded over 4 months with no major process upsets. After 1 and 2 months, a single sample holder was removed from the oven. At 4 months, the two remaining samples were removed. The duplicate samples at 4 months allowed for evaluation of the reproducibility of the results. After each sample was removed from the oven, it was purged with dry air at room temperature for 1 week to remove any iodine that may have desorbed during aging, along with any residual NO_2. Following air purge, each sample was analyzed for iodine by neutron activation analysis.

4. CONCLUSIONS

The aging study was completed successfully. The material did not visibly change color or form. Neutron activation results are shown in Table 1. There is some variability observed within the iodine loadings, and this is most likely due to uneven loading within the deep bed test system. However, these results do demonstrate that no significant iodine loss was observed over the course of 4 months of 2% NO_2 aging of I_2-Ag^0Z at elevated temperature. This provides assurance that iodine will remain immobilized on Ag^0Z during extended online use in an off-gas capture treatment system. Future tests should expose I_2-Ag^0Z to progressively more complex feed gases in an effort to accurately replicate the conditions expected in a reprocessing facility.

Table 1. Post-aging iodine loadings

Aging Time (months)	I_2 Loading (wt %)	Uncertainty (wt %)
0	7.15	0.10
1	8.90	MDA
2	7.71	MDA
4a	7.78	0.014
4b	7.44	0.012

(MDA: Minimum Detectable Activity)

5. REFERENCE

Jubin, R. T. 2011. *Report of the FY11 Activities of the Off-Gas Sigma Team*, FCR&D-SWF-2011-000306, U.S. Department of Energy Separations and Waste Forms Campaign, September.