Stability of Tritium and Iodine Sorbents under Tritium-Pretreatment Off-Gas Conditions

Nuclear Technology Research and Development

Prepared for
U.S. Department of Energy
Material Recovery and Waste Form Development Campaign
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31 March 2017
ORNL/SR-2017/162
NTRD-MRWFD-2017-000411

SUMMARY

US regulations could require the removal of both iodine and tritium from the off-gas stream of a used nuclear fuel (UNF) reprocessing facility. Advanced tritium pretreatment is a pretreatment step that uses high concentrations of NO_2 in a gas stream to volatilize tritium and iodine from UNF prior to traditional dissolution. The gaseous effluent from this process would then require abatement to remove tritium and iodine, but high levels of NO_2 could have a detrimental effect on the ability of various solid sorbents to remove the volatile radionuclides. For tritium and iodine, the sorbents of interest are 3Å molecular sieve (3AMS) for tritium and reduced silver mordenite (Ag^0Z), silver-functionalized silica-aerogel (AgAerogel), and silver-nitrate-impregnated alumina (AgA) for iodine. Prior research has demonstrated that exposure to high concentrations of NO_2 can reduce the iodine loading capacity of Ag^0Z by > 90% when exposed for 1 week. Research in Japan has demonstrated that AgA is more robust to NO_2 exposure than AgZ. The testing described here was intended to assess the effects of high concentrations of NO_2 on the iodine capture capacity of AgA and the water adsorption capacity of 3AMS.

To determine the effect of extended exposure of the sorbents to NO_2, both 3AMS and AgA were aged in a 75% NO_2 environment prior to loading. The 3AMS samples were aged for 1, 4, and 5.5 weeks at 40°C. They were then loaded with water in a 10°C dew point stream (corresponding to a water concentration of ~12,000 ppmv) at 40°C. There was no significant change in the water adsorption capacity of the 3AMS upon exposure to 75% NO_2.

The AgA samples were aged for 1, 2, and 4 weeks at 150°C and were loaded with 50 ppmv I_2 at 150°C. The results show that the iodine capture capacity of AgA is reduced by exposure to high concentrations of NO_2. The iodine capacity reductions were 16%, 36%, and 76% for 1, 2, and 4 week exposures, respectively. This is less of a capacity loss than that seen in similar testing with the Ag^0Z sorbent.

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ACRONYMS

3AMS	3Å molecular sieve
AgA	silver-nitrate-impregnated alumina
AgAerogel	silver-functionalized silica-aerogel
Ag^0Z	reduced silver-exchanged mordenite
ATPOG	advanced tritium-pretreatment off-gas
ATPT	advanced tritium pretreatment
DF	decontamination factor
EDS	energy-dispersive x-ray spectroscopy
NAA	neutron activation analysis
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
TPOG	tritium-pretreatment off-gas
TPT	tritium pretreatment
UNF	used nuclear fuel
XRD	x-ray diffraction

STABILITY OF TRITIUM AND IODINE SORBENTS UNDER TRITIUM-PRETREATMENT OFF-GAS CONDITIONS

1. INTRODUCTION

Current US regulations require the treatment of off-gas from used nuclear fuel (UNF) reprocessing to remove several radioisotopes. Specific volatile radionuclides (e.g. iodine-129 and krypton-85) have explicit maximum release limits. Further reduction in the releases may also be required for them and for other volatile radionuclides so that the overall whole-body and thyroid dose limits for the public are not exceeded. Based upon these dose limits, Jubin et al. (2012) concluded that the treatment of the off-gas to capture tritium may be required in addition to the capture of iodine.

Typically, iodine is evolved into the off-gas primarily during the fuel dissolution step where > 90% is released into the off-gas (Hermann et al. 1997). Since iodine is not fully released into the dissolver off-gas during dissolution, a significant fraction of the balance will be released into other plant off-gas streams. Those streams may also require treatment.

In current reprocessing facilities the tritium present in the fuel is retained in the dissolver solution primarily as HTO and is distributed throughout the facility. It may be possible to prevent the spread of tritium through the plant by adding a pretreatment step prior to dissolution that can quantitatively remove tritium from the UNF. A dry process was developed in the 1960s, referred to as voloxidation, or more recently as tritium pretreatment (TPT), in which oxygen converts the UO_2 in the fuel pellets to U_3O_8. The oxidation step and crystal restructuring result in the formation of a fine powder and in the release of tritium. A variation of this process, designated advanced TPT (ATPT), uses NO_2 as the oxidant instead of O_2. This process variation appears to result in a significant iodine release. The off-gas from ATPT, referred to as advanced tritium pretreatment off-gas (ATPOG), contains high NO_2 concentrations (75%) as well as iodine, tritium, and other volatile species. The introduction of high NO_2 concentrations (75%) to the gas stream requiring treatment may add complexity to the off-gas removal system due to the potential deleterious effects of the NO_2 on the sorbents intended for use in tritium and iodine removal.

Recent research into gaseous iodine sorption has investigated reduced silver mordenite (Ag^0Z) as a potential iodine sorbent. Ag^0Z can adsorb iodine with a sorption capacity in the range of 100 mg iodine/g sorbent or greater (depending on the silver content of the material). However, when Ag^0Z was exposed to 75% NO_2 prior to iodine loading, the iodine capture capacity was reduced by up to 97% (Jubin et al. 2013). Based on those tests, alternate iodine sorbents would appear to be required for the ATPT scenario.

One alternative iodine sorbent is silver-functionalized silica aerogel (AgAerogel), provided by researchers at Pacific Northwest National Laboratory for testing at Oak Ridge National Laboratory. AgAerogel can achieve iodine loadings of ~330 mg iodine/g for sorbent with ~35 wt % silver. The material was exposed to a 2% NO_2 environment for 4 months; samples were taken in month intervals. The iodine loading on AgAerogel was largely unaffected after 1 month of exposure (or “aging”), but 4 months of exposure resulted in a 14.5% loss in iodine capture capacity (Patton et al. 2014). This material was not exposed to higher NO_2 concentrations.

Another candidate sorbent for iodine removal is silver-nitrate-impregnated alumina (AgA), primarily tested by researchers in Japan (Hattori et al. 1984, Fukusawa et al. 1994). Hattori et al. (1984) reported that iodine capacity was not affected when loaded in the presence of 1 vol % NO_2. Fukusawa et al. (1994) noted a drop in the decontamination factor (DF) achieved across a bed of fixed length when the sorbent is loaded in the presence of > 70% NO_2. However, it is unclear from the reported data how the decrease in DF corresponds to iodine loading capacity.

One of the primary sorbents for water adsorption is 3Å molecular sieve (3AMS), which has a theoretical water loading capacity of ~180 mg H_2O/g 3AMS (according to the GRACE-Davison Isotherms (GRACE 2010) at a water feed concentration of 12,120 ppmv (40°C dew point) and a temperature of 40°C.

The research documented in this report was carried out to determine the effects of NO_2 exposure on the sorption capacities of 3AMS and AgA. Samples were aged in a 75% NO_2 environment at an elevated temperature. AgAerogel was not aged at the high-NO_2 concentration in this work; the low-concentration results suggest a resistance to deleterious NO_2 aging effects. The aging in this work is static aging, where the sorbent material is stored in an NO_2 environment for a given time prior to iodine loading rather than in a flowing stream containing NO_2 or NO_2 and the desired adsorbate. The Japanese literature utilizes “dynamic” aging, where the sorbent is loaded with iodine in a stream that also contains NO_2 of the desired concentration. The latter method is more representative of what would be expected in a real reprocessing stream, although static aging can still provide useful information regarding the effect of NO_2 exposure.

Future work will examine the impacts of aging on material structure and composition. The samples will be analyzed by x-ray diffraction (XRD) and scanning electron microscopy – energy-dispersive x-ray spectroscopy (SEM-EDS).

The information provided in these experiments will inform the design of the system to remove tritium and iodine under ATPOG conditions described by Spencer et al. (2017).

2. Experimental Procedures

AgA was prepared from commercially available alumina and silver nitrate solution (Sect. 2.1). 3AMS was used as received from the manufacturer. The aging of the materials is described in Sect. 2.2, and the loading of the aged 3AMS with water and the aged AgA with iodine is discussed in Sect. 2.3.

2.1 Preparation of Silver-Exchanged Alumina

AgA was prepared by coating commercially available alumina spheres (Sorbent Technologies) with silver nitrate. A sample consisting of 500 g of alumina spheres was added to a solution of 125 g of $AgNO_3$ in 380 mL of distilled water; the solution was heated under vacuum in a rotary evaporator for 9 h at 125°C.

2.2 Aging

The AgA and 3AMS were aged in sample holders (Fig. 1). Three sample holders were loaded with 10 g of 3AMS, and three sample holders were loaded with ~10 g of prepared AgA. Once the material was loaded into the sample holders, the sample holders were then evacuated, filled with 100% NO_2 gas, and then diluted with dry air to achieve the desired NO_2 concentration. The sample holders were then placed in an oven for varying amounts of time. The temperatures of aging were the same as the temperatures to be used in sorbent loading. The 3AMS was aged for 1, 4, and 5.5 weeks at 40°C; the AgA was aged for 1, 2, and 4 weeks at 150°C.

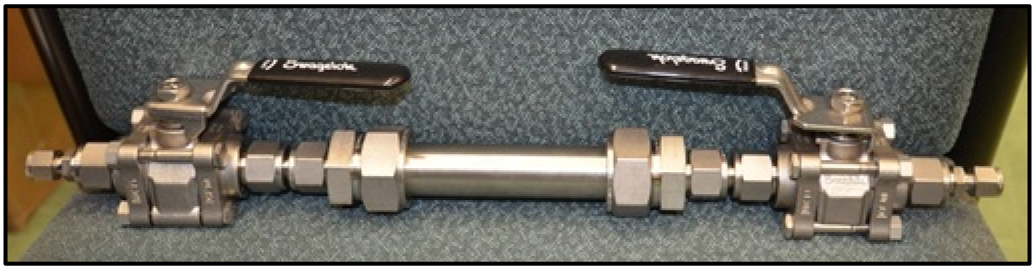

Figure 1. Sample holder for aging.

After the samples aged for the desired length of time, the sample holder was purged with dry air at 2 LPM for 1 h to remove residual NO_2 (this results in > 2,600 volume changes). The samples were then stored in sample vials. The 3AMS did not appear to undergo any visible physical change (Fig. 2), but the AgA changed color from a primarily dark gray to white (Fig. 3). The cause of this color change has not yet been determined. Future work will utilize EDS to attempt to characterize this change.

The aged sorbents samples were split, with a portion of the sample designated for loading tests and a portion designated for analysis using XRD, SEM, and EDS.

Figure 2. 3AMS material. L–R: unaged; aged 1, 4, and 5.5 weeks.

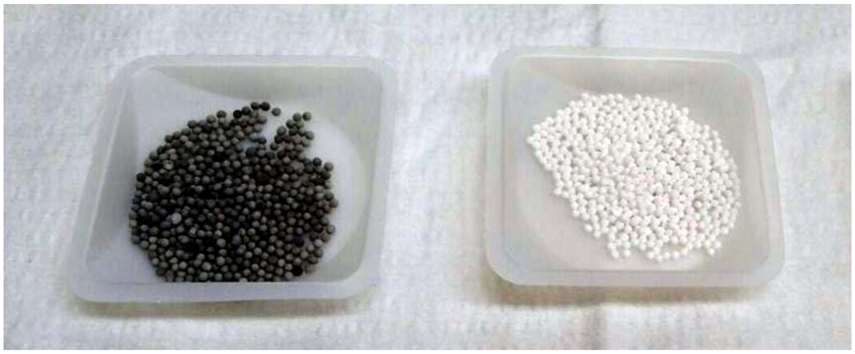

Figure 3. AgA material. L-R: unaged, aged 1 week.

2.3 Weight Gain Measurements

The aged materials were loaded with the gas constituent of interest—iodine for AgA and water for 3AMS—to compare the loading behavior before and after exposure to NO_2.

Adsorption capacities for iodine and water were measured using a thermogravimetric analyzer (TGA). Each test consisted of a sorbent sample placed in a basket within an oven, where the weight of the basket was continuously measured. Gas was flowed through the sample basket allowing for the detection of weight changes in the sample when exposed to the feed gas. The general procedure for these tests is as follows:

1) The sample is first placed in the oven and is exposed to a flowing stream of dry air (-70°C dew point) until fully equilibrated as measured by stable weight.
2) The composition of the gas stream is then modified with the addition of iodine or water at the desired concentrations while a constant flowrate is maintained. The loading period lasts until no further weight change is observed (i.e., the end of loading).
3) The gas stream is again modified to a dry air stream to remove physisorbed iodine in the case of AgA or to track the water desorption from the 3AMS.

The dry air is treated by passing the plant air through a Drierite bed followed by a bed of 3AMS to reduce the dew point to < -60°C. The run conditions for the loading tests can be seen in Table 1. The difference in temperature is due to a difference in preferred loading conditions. Iodine sorption on AgA is enhanced at 150°C. The 40°C loading temperature for the 3AMS was chosen to represent a compromise between possible operating conditions necessitated by the process (likely to be higher temperature) and ideal temperature for water loading (lower temperature).

Table 1. Run conditions for TGA loading.

	AgA	**3AMS**
[I_2] (ppmv)	50	0
Water dew point (°C)	< -60	10
Temperature (°C)	150	40
Gas velocity (m/min)	10	2.5

3. Results

The samples were loaded as previously described, either with water on 3AMS or iodine on AgA.

3.1 Water on 3AMS

Water loading on 3AMS is presented in Fig. 4 for the unaged, 1-week-aged, 4-week-aged, and 5.5-week-aged material. The final loading capacity was similar for all four runs, ranging from 149.3 to 155.7 mg H_2O/g 3AMS. Prior experience suggests that these loading values are all within the error of the TGA. Thus loading does not appear to have been affected by exposure to NO_2, although there may be some slight decrease in the adsorption rate for the NO_2-aged materials. The unaged sample contained 10 mg/g more water than the 5.5-week-aged sample at 1 h and nearly 20 mg/g more at 2 h. The unaged sample reaches its final loading in about 4 h; the aged samples require ~ 6 h. The desorption curves (Fig. 5) are presented separately from the loading curves to normalize the graphs based on time of initial purging. As with the loading curves, there do not appear to be discernable differences in the desorption process.

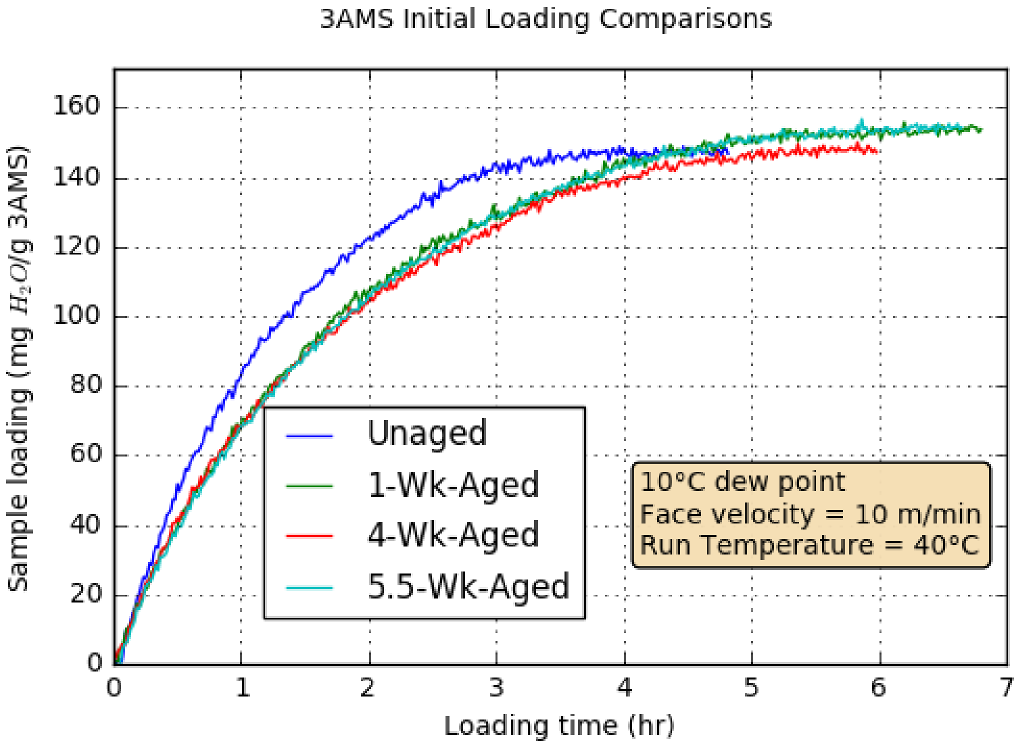

Figure 4. Comparison of water loading on 3AMS for sorbents of various time-exposure to NO_2.

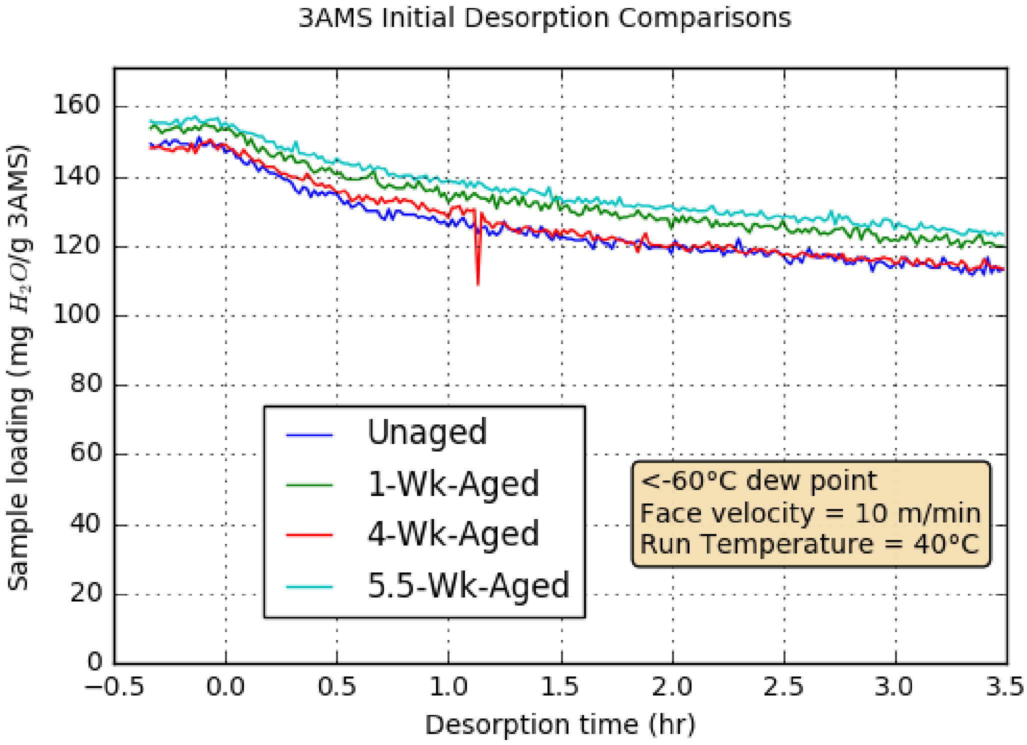

Figure 5. Desorption curves for water on 3AMS for sorbents aged in NO_2.

3.2 Iodine on AgA

Iodine loading on AgA is presented in Fig. 6. The final iodine loading capacity was reduced from 101 to 24 mg I_2/g AgA from the unaged to the 4-week-aged material, with intermediate values falling within that range. These samples were examined with neutron activation analysis (NAA) to assess iodine content (Table 2). The NAA agreed closely with the TGA results with the exception of the 4-week-aged sample, in which case the NAA showed only a ~50% reduction in loading compared to the ~75% observed reduction based on the TGA results.

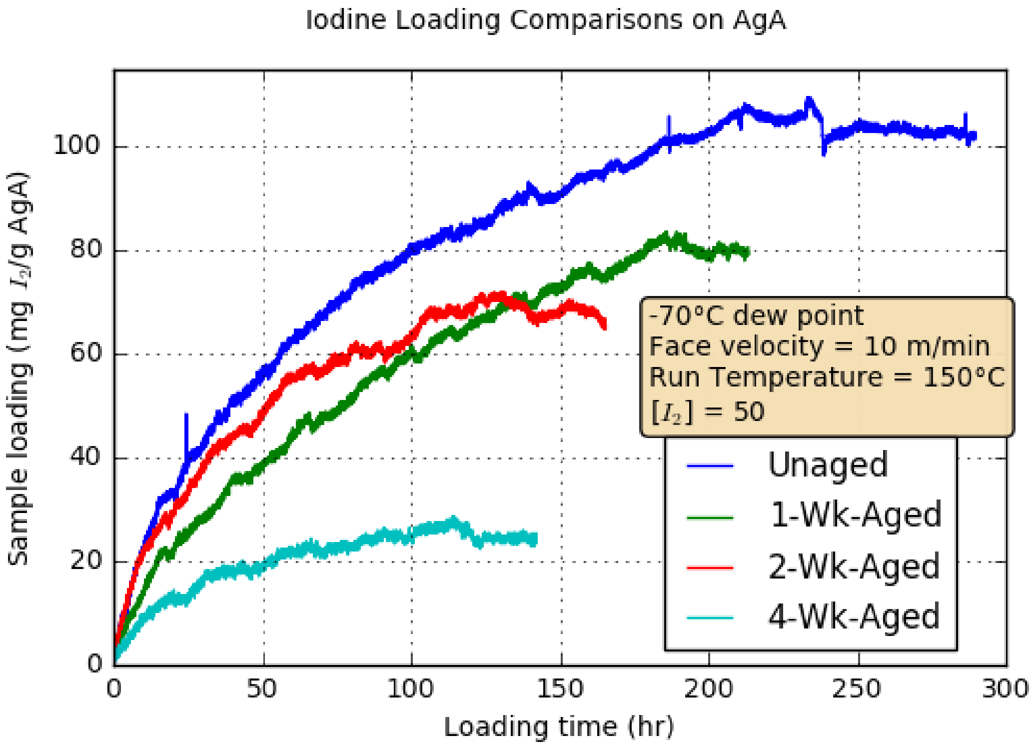

Figure 6. Comparison of iodine loading on AgA.

Table 2. Final loading comparison between weight estimate and NAA.

	Iodine loading capacity (mg/g)	
Aging time	TGA weight gain	NAA
No aging	101	98
1 week NO_2	85	79
2 week NO_2	64	69
4 week NO_2	24	48

4. Conclusions

The capacities of high-NO_2-concentration aged materials were determined by loading experiments using a TGA. There is no measureable effect of NO_2 aging on the water adsorption capacity of 3AMS. The loading rate of water on 3AMS decreased slightly upon exposure to NO_2 prior to loading.

The effect of NO_2 exposure for 4 weeks on AgA results in a reduction of ~ 50% to ~ 75% in the iodine loading capacity. It is not possible to compare these numbers directly to the Japanese research results as Fukusawa et al. (1994) did not provide specific values for NO_2 exposure or capacity loss, instead reporting the decrease in DF across an AgA bed of a given length. However, the decrease in iodine capacity shown in these tests could lead to the decline in DF observed by the Japanese researchers. To aid in direct comparison, future work could utilize dynamic NO_2 exposure, as opposed to the static exposure used in this work.

It is also useful to compare the effect of NO_2 aging of AgA to similar studies with Ag^0Z and AgAerogel. 4 week aging of AgA resulted in a capacity loss of ~75% for iodine capture; 4 week aging of Ag^0Z resulted in a 92% capacity loss. 1 week aging of these materials resulted in a capacity loss of 16% for AgA and 97% Ag^0Z. Direct comparisons of this study with AgAerogel aging studies are not possible as AgAerogel was aged in a 2 vol % NO_2 environment. AgAerogel does not lose capacity when aged under those conditions for 1 month. This apparent resistance of AgAerogel to NO_2 at low concentrations is promising for future work.

AgA appears to be more resistant to NO_2 than Ag^0Z, which confirms the results of previous research (Hattori et al. 1984). Future work in this analysis will include elemental mapping of the material with SEM-EDS and XRD with a goal of identifying potential mechanisms that would explain the differences in behavior to the NO_2 exposure.

The change in iodine loading capacity of AgA could be related to the color change observed upon exposure to the NO_2 environment (Fig. 3). The precise reason for the color change is unknown and merits future study. This future work should include determination of the changes in sorbent structure and the precise state of the silver.

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