Determination of Mechanisms and Kinetics of Ag^0Z and Ag^0-Aerogel Aging in Nuclear Off-Gases

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INTRODUCTION

Radiological iodine (^{129}I) gas removal from the used nuclear fuel reprocessing off-gas stream is crucial due to its high mobility, long half-life, and bioaccumulation. Ag containing adsorbents are highly effective for capturing radiological iodine due to the strong affinity of silver for iodine. Ag-exchanged mordenite (Ag^0Z) and Ag-functionalized silica aerogel (Ag^0-aerogel) are outstanding adsorbents and have been extensively studied. However, one problem exists with Ag containing adsorbents which is the deactivation of Ag during the long-term exposure (up to 6 months) to the off-gas stream containing H_2O, NO and NO_2. To address this problem, the "aging" process of the adsorbents in off-gases should be well understood.

Previous studies have experimentally investigated the aging of Ag^0Z and Ag^0-aerogel in off-gases and found that their capacity for iodine adsorption decreased significantly under most of the studied aging conditions.[1-10] For example, Ag^0Z lost 60% of the capacity after aging in a humid-air flow for 4 months and lost 78% of the capacity after aging in a batch reactor filled with 1% NO/air for 2 months, and under the same conditions Ag^0-aerogel lost 22% and 43% of the capacity, respectively. The results indicated that Ag^0Z and Ag^0-aerogel had different aging behaviors in the off-gases. However, mechanisms of the processes are not clear. To understand the aging process, the mechanisms and kinetics of the process must be studied.

Towards this objective, aging experiments were conducted to determine the mechanisms of the aging processes of Ag^0Z and Ag^0-aerogel in off-gases. Iodine adsorption experiments were also performed to obtain data for studying the kinetics of the process. In addition, work is on-going to develop models describing the deactivation process of the adsorbents when exposed to off-gases. The deactivation model will be included in the transport models for predicting the adsorption processes over long periods.

DATA ACQUISITION AND ANALYSIS

Aging experiments were conducted in off-gas species including dry-air, humid-air (dew point of -15°C), 1% NO/N_2 and 2% NO_2/air, respectively, using a continuous-flow aging system as shown in **Fig 1**. The Ag^0Z and Ag^0-aerogel were aged in the glass columns inside the ovens at 150 °C. There are four columns in each oven corresponding to the four off-gases. Each column has four sections that could be aged for different periods of time. The gases were passed through the columns at high flow rates to ensure that the gas concentration was uniform throughout each column.

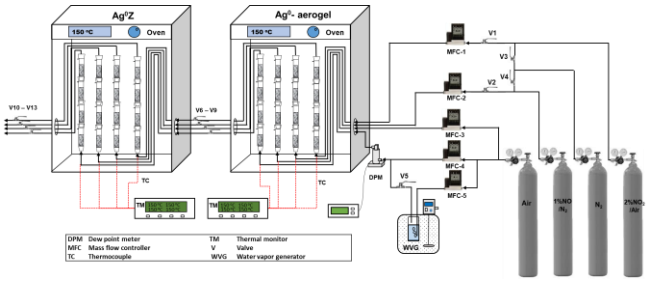

Fig. 1. The continuous-flow aging system.

The collected samples were analyzed by using various methods including SEM (scanning electron microscopy) and ASAP 2020 surface area and porosity analyzer to determine the physical changes; and X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption fine structure (XAFS) to determine changes in chemical composition and oxidation states of Ag upon aging.

In addition, I_2 adsorption experiments were conducted with the aged samples to determine the iodine adsorption capacities and obtain kinetic data of the aging process. The continuous-flow iodine adsorption systems were described previously.[6] The kinetic data of the aging process as well as the uptake curves of I_2 adsorption on aged adsorbents were used to develop adsorption models that include aging effects.

Our previous work has evaluated and developed models to predict multicomponent adsorption equilibria[7-8] and mass transfer kinetics in porous pellets.[9] These developed models are capable of predicting the adsorption rates of iodine without aging issues (**Fig 2**). To adapt these models for iodine adsorption on Ag^0Z and Ag^0-aerogel, chemical and physical/structural changes to the adsorbents, as well as aging effects, need to be included. For example, the oxidation of the Ag sites within the adsorbent will affect the maximum adsorption capacity, and structural changes, including losses in porosity, surface area, and pore size, would lead to retardation of the overall uptake of material into the adsorbent structure.

RESULTS

Chemical analyses performed in this study indicated that when Ag^0Z was exposed to dry air, humid air, NO and

NO_2, the reduced Ag^0 in Ag^0Z was oxidized to Ag^+. However, no Ag oxides or nitrated Ag were detected on the aged Ag^0Z. The XRD patterns (**Fig. 3**) and SEM images (**Fig. 4**) of NO_2 aged Ag^0Z are shown as an example. Results of XPS and XAFS showed that the Ag^+ in the aged Ag^0Z were in the same oxidation state as in AgZ, indicating that the oxidized silver (Ag^+) migrated into the pores of mordenite crystals. As for Ag^0-aerogel, the chemical analyses indicated that when exposed to dry air, humid air and NO, the Ag^0 in Ag^0-aerogel was oxidized and formed Ag_2S, while the exposure to NO_2 formed Ag_2SO_4. The generated Ag_2S and Ag_2SO_4 crystals were observed on the surface of the aerogel.[10]

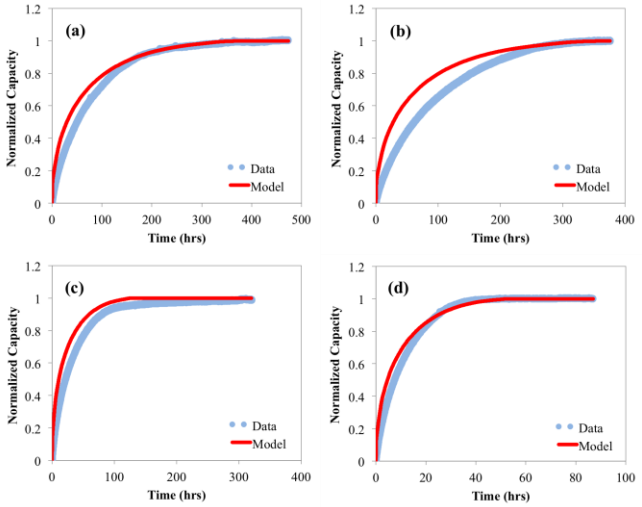

Fig. 2. Iodine uptake rate predictions in Ag^0Z pellets at various temperatures (T) and iodine concentrations (C), without aging effects. (a) T = 100 °C and C = $1.3x10^{-3}$ kPa, (b) T = 150 °C and C = $1.4x10^{-3}$ kPa, (c) T = 150 °C and C = $3.7x10^{-3}$ kPa, and (d) T = 200 °C and C = $8.8x10^{-3}$ kPa.

According to the results of the chemical and physical analyses, the mechanisms of Ag^0Z and Ag^0-aerogel aging in the off-gases were determined. For example, the pathways of Ag^0Z aging in NO_2 are:

$$2NO_2 + 8Ag \rightarrow 8Ag^+ + 4O^{2-} + N_2 \quad (1)$$

(followed by migration of Ag^+ into the micropores)

$$Ag^+ + HZ \rightarrow AgZ + H^+ (Z = Mordenite) \quad (2)$$

$$2H^+ + O^{2-} \rightarrow H_2O \quad (3)$$

$$\text{Overall: } 2NO_2 + 8Ag + 8HZ \rightarrow 8AgZ + 4H_2O + N_2 \quad (4)$$

Details of all mechanisms will be disussed in the presentation.

The iodine adsorption capacity of the aged Ag^0Z and Ag^0-aerogel were determined through experiments of I_2 adsorption. The iodine adsorption capacity loss over aging time is summarized in **Fig 5**.[11] It was found that Ag^0Z had significant reductions in capacity when exposed to off-gases, especially to NO_x which resulted in a >90% relative capacity loss. Ag^0-aerogel was noted to have a higher resistance to air, H_2O and NO than AgZ with 10%-20% relative capacity loss after 6-month exposure. However, in NO_2, it still lost more than 90% of iodine adsorption capacity within 1 month.

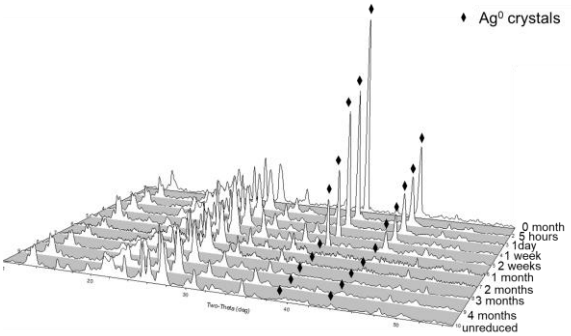

Fig. 3. XRD patterns of NO_2 aged Ag^0Z for different periods and AgZ.

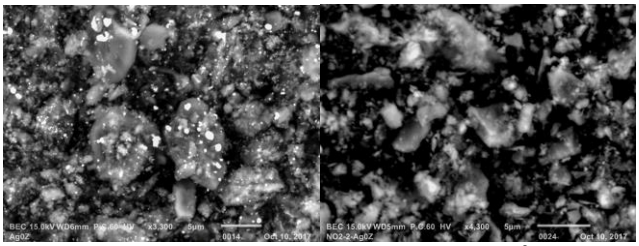

Fig. 4. SEM (backscatter electron) image for Ag^0Z (left) and Ag^0Z aged in NO_2 for 2 months (right). The bright dots observed on the Ag^0Z image are Ag^0 particles which are not found on the NO_2 aged Ag^0Z.

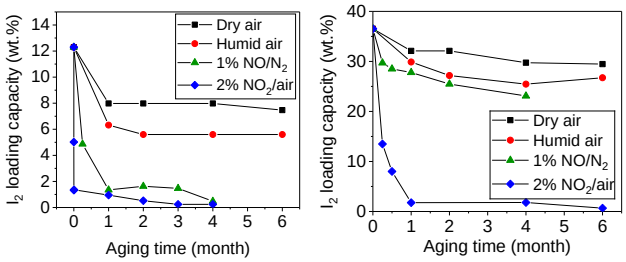

Fig. 5. Iodine adsorption capacity of Ag^0Z (left) and Ag^0-aerogel (right) as a function of aging time.

To obtain kinetic data for model development, short-time aging experiments are conducted (on-going). Current results shown in **Fig. 6** indicate that Ag^0Z has fast aging processes in humid air and NO_X, especially in NO_2, where >90% of the capacity is lost within an hour. The aging of Ag^0-aerogel was found slower than Ag^0Z due to the different aging mechanisms. Kinetic data will also be obtained at temperatures of 100 °C and 200 °C. Models will be developed to describe the reaction and mass transfer involved in the aging kinetics.

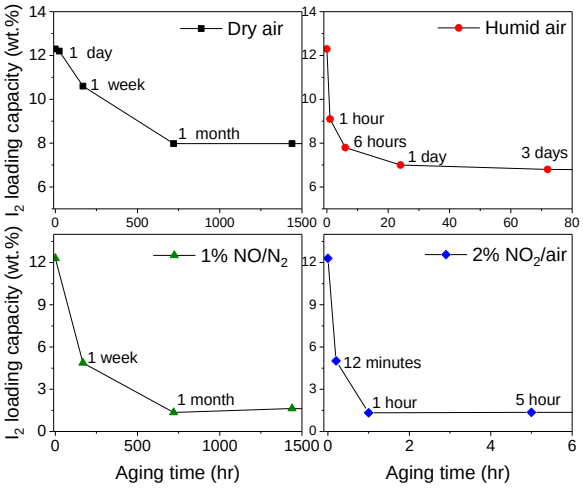

Fig. 6. Kinetic data of Ag^0Z aging in dry air, humid air (dew point of -15ºC), 1% NO/N_2 and 2% NO_2/air at 150 ºC.

CONCLUSIONS

The determination of the aging mechanisms and kinetics will provide valuable information to better understand the performance of the adsorption systems and better design of the iodine capture systems. The obtained aging kinetic data and iodine adsorption data ensure high accuracy in developing fundamental models to predict the adsorption process including aging effects. These models can be incorporated into complex adsorption column models for the simulation of off-gas adsorption systems.

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