ABSTRACT

Filtered containment venting system (FCVS) is an emergency response system for severe accident. FCVS reduces the pressure in reactor vessel and removes radioactive iodine and cesium.

Recently, silver doped zeolite (AgX) has been attracting attentions since it is believed to remove over 99.99% of CH\textsubscript{3}I in the ventilation gas. However, the reliable data of AgX for CH\textsubscript{3}I sorption under expected severe accident conditions are still limited. Therefore, the sorption behavior of CH\textsubscript{3}I on AgX was investigated under several expected conditions.

In this study, the CH\textsubscript{3}I labeled by 125I tracer was synthesized by isotope exchange reaction, and it was devoted for sorption experiment on AgX. Sorption experiment using stable CH\textsubscript{3}I was also conducted by the same procedure. From results of the sorption experiment, over 99.9% of 2.28g of CH\textsubscript{3}I were sorbed by 10g of AgX. After the sorption experiment, AgX samples were analyzed by powder X-ray diffraction (XRD) and SEM-EDX. These results indicated the distribution of Ag agreed with that of I in micro area of AgX. For the evaluation of apparent sorption capacity of AgX, breaking through experiment was carried out. The apparent sorption capacity of AgX for CH\textsubscript{3}I was determined as 0.25g / g (AgX) at 24°C. The breaking through experiment was also carried out for the evaluation of CH\textsubscript{3}I flux and humidity effects in the vent gas. The effect of temperature on the sorption capacity was also studied. When the flux of CH\textsubscript{3}I supply was increased from 1.09 × 10\textsuperscript{-4} to 2.33 × 10\textsuperscript{-4}g/cm\textsuperscript{2}s, apparent sorption capacity was unchanged (=0.21g / g (AgX)). Besides, the apparent sorption capacity was unchanged in the humidity range of ~0 % H\textsubscript{2}O to 0.01 % H\textsubscript{2}O, while it decreased to 0.19 g / g (AgX) at 3% H\textsubscript{2}O. When sorption temperature increased to 170°C, the apparent sorption capacity also increased to 0.69 g / g (AgX).

1. INTRODUCTION

In the severe accident of Fukushima Daiichi Nuclear Power Station, a huge amount of radioactive materials such as cesium and iodine were released from the reactor to environment. The release of radioactive materials should have been controlled as low as possible for preventing public exposure and health hazard. Filtered containment venting system (FCVS) is an emergency response system for severe accident. It is designed to remove radioactive I and Cs released from the reactor vessel at the severe accident [1-2]. Iodine exists as different chemical species such as I\textsubscript{2} and CH\textsubscript{3}I in gas phase and I\textsuperscript{-} and IO\textsubscript{3}\textsuperscript{-} in liquid phase. I\textsubscript{2} in ventilation gas easily dissolves in water and fixed by sorbent like other water soluble ions. However, this kind of sorption system does not work for water insoluble species such as CH\textsubscript{3}I. The silver doped zeolite (AgX) is regarded as very promising sorbent for CH\textsubscript{3}I since it can remove over 99.99% of CH\textsubscript{3}I in the vent gas [3]. However, the reliable experimental data of AgX for CH\textsubscript{3}I sorption is still quite limited. So we carried out the advanced sorption experiment of it. In this study, sorption of radioactive CH\textsubscript{3}I synthesized by isotope exchange reaction was examined by using AgX. In the breaking through experiment, the sorption capacity of AgX for CH\textsubscript{3}I was evaluated under some experimental conditions. After that, the AgX samples were analyzed by XRD and SEM-EDX to investigate the mechanism of this sorption.
2. EXPERIMENTAL

2.1 Synthesis of radioactive methyl iodide

The CH₃I labeled by ¹²⁵I was synthesized by the following isotope exchange reaction between alkaline solution of Na₁²⁵I and CH₃I [4];

\[ \text{Na}^{125}\text{I} + \text{CH}_3\text{I} \rightleftharpoons \text{CH}_3^{125}\text{I} + \text{NaI}. \] (1)

First, 0.5 ml or 1.5 ml of 0.1 M NaOH solution containing trace amount of Na₁²⁵I was contacted with 2.5 ml of reagent grade CH₃I (which is liquid state at the room temperature) in a glass vial, where the 0.1 M NaOH solution and CH₃I were clearly separated. Then two phases were mixed by a magnetic stirrer with light shielding. After the mixing, two phases were re-separated and NaOH solution was removed from the vial, then, 0.1 ml of the CH₃I was sampled and diluted by 0.9 ml of ethanol for the γ-activity measurement. The γ-activity was measured by a sodium iodide scintillation spectrometer (NaI). From the result, we calculated the exchange ratio. The exchange ratio (R) was calculated using the following equation;

\[ R = \frac{W_2}{W_1} \times \frac{V_2}{V_1}, \] (2)

where R : Sorption ratio (%), W₁ : Counts of ¹²⁵I injected (cps/ml), W₂ : Counts of ¹²⁵I exchanged to CH₃I (cps/ml), V₁ : Volume of Na₁²⁵I (ml), V₂ : Volume of CH₃I (ml).

2.2 Sorption experiment

Sorption experiment was carried out using radioactive CH₃¹²⁵I and stable CH₃I. Figure 1 shows overview of the experimental system. The experimental apparatus were made by PYREX glass to prevent the loss of CH₃I by adhering inside. The system consists of four parts, i.e. 1) CH₃I injection part, 2) Tube 1: sorption tube with AgX doped zeolite, 3) Tube 2: recovery tube for un-trapped CH₃I and 4) Tube 3: additional recovery tube for un-trapped CH3I. 15ml of 99 wt% ethanol and 15ml 50 wt% ethanol were filled in Tube 2 and 3, respectively to trap CH₃I passed through AgX column (= Tube 1). 1.0 ml of CH₃I or CH₃I was injected and carried to Tube 1 by carrier gas (Ar). Gas flow rate was set to 20 ml / min. After the experiment, the trap solutions in Tube 2 and 3 were sampled for the measurement of I by ICP-AES. From the result, we calculated the sorption capacity of AgX. Experiments were also carried out for evaluation of humidity effect on the sorption, humidity in the carrier gas was changed from 0 to 3% H₂O by changing carrier gas from pure Ar to Ar + 100 ppm H₂O (=0.01 % H₂O) or Ar through water bubbler (= 3% H₂O). For the evaluation of the effect of sorption temperature on the sorption, temperature of Tube 1 was changed from 24°C to 170°C.

2.3 Breaking through experiment

Breaking through experiment was carried out to evaluate the apparent sorption capacity of AgX. A hundred µl of stable CH₃I was supplied to AgX in the Tube 1 repeatedly until its breaking through. The Ar carrier gas was introduced at a flow rate 20 ml / min and temperature was set to 24°C. The trap solutions of Tubes 2 and 3 were sampled for the measurement of I by ICP-AES. From the result, we calculated the apparent sorption capacity of AgX. Experiments were also carried out for evaluation of CH₃I flux change, humidity in the carrier gas and sorption temperature on the sorption capacity. For the evaluation of CH₃I flux effect, it was changed from 1.09×10⁻⁴g/cm²s to 2.33×10⁻⁴g/cm²s by controlling CH₃I vapor pressure. The Ar flow rate was set to 20 ml / min. For the evaluation of humidity effect on the sorption, humidity in the carrier gas was changed from 0 to 3% H₂O by changing carrier gas from pure Ar to Ar + 100 ppm H₂O (=0.01 % H₂O) or Ar through water bubbler (= 3% H₂O). For the evaluation of the effect of sorption temperature on the sorption, temperature of Tube 1 was changed from 24°C to 170°C.

2.4 XRD and SEM-EDX analyses

After the sorption experiment, AgX samples were analyzed by powder X-ray diffraction (XRD) by Rigaku Miniflex II system using Cu-Kα radiation to identify the chemical form of sorbed iodine in the AgX. XRD patterns of before and after the sorption experiment were measured and compared each other. For SEM-EDX analysis, Hitachi SU-1000 system was used. AgX samples after the sorption experiment were encapsulated by epoxy resin then, coated by Au-Pd spattering.

3. RESULTS AND DISCUSSION

3.1 Synthesizing radioactive methyl iodide

The labeled CH₃I by ¹²⁵I was synthesized by the isotope exchange reaction. Figure 2 shows the isotope exchange ratio of synthesized radioactive methyl iodide. The exchange ratio
increased with increasing contacting time. At 68 h, more than 15% of supplied $^{125}$I as Na$^{125}$I was exchanged to CH$_3^{125}$I.

![Graph showing isotope exchange ratio from Na$^{125}$I to CH$_3^{125}$I.](image)

**Fig. 2** Isotope exchange ratio from Na$^{125}$I to CH$_3^{125}$I.

### 3.2 Sorption experiment

When the amount of AgX in Tube 1 was increased, the sorption ratio of CH$_3$I was increased. Over 99.9% of CH$_3$I were sorbed by 10g of AgX. The result shown in Figure 3 indicates that both labeled CH$_3^{125}$I and stable CH$_3$I showed similar sorption behavior.

![Graph showing relation of sorption ratio and amount of AgX.](image)

**Fig. 3** Relation of sorption ratio and amount of AgX. (Temperature: 24°C, Carrier gas: Ar, Flow rate: 20ml/min)

Figure 4 shows color change of AgX during the sorption experiment. In the progress of CH$_3$I sorption, color of AgX changed from white to yellow gradually.

![Images showing color change of AgX before and after experiment](image)

**Fig. 4** Color change of AgX in the sorption experiment.

### 3.3 XRD and SEM-EDX analyses

The XRD patterns of the AgX before and after the CH$_3$I sorption are shown in Figure 5, where XRD pattern of reagent AgI is also shown for comparison. As shown in Figure 6, typical peaks of AgI are found in Fig. 5-(ii) (= after sorption) which are not found in Fig. 5-(i) (=before the sorption), indicating the formation of AgI is by the sorption of CH$_3$I on AgX.

![XRD analysis patterns for (i) AgX before sorption, (ii) AgX after sorption, (iii) Reagent AgI](image)

**Fig. 5** XRD analysis patterns for (i) AgX before sorption, (ii) AgX after sorption, (iii) Reagent AgI

Figure 6 shows images of element mapping by SEM-EDX. It can be seen that the main components of AgX, i.e., Ag, Al and Si were affected and distributed homogeneously, and iodine took the same distribution with matrix elements of AgX.

From the results of XRD and SEM-EDX analyses, we concluded the sorption of CH$_3$I progressed homogeneously in the particle of AgX by forming AgI. The sorption mechanism of CH$_3$I on AgX is expected to be:

$$2CH_3I + 2Ag \rightarrow 2AgI + C_2H_6.$$  \hspace{1cm} (3)
3.4 Breaking through Experiment

Figure 7 shows the result of breaking through Experiment, where temperature was 24°C and carrier gas was Ar in flow rate 20ml/min. Almost all of CH₃I were sorbed by AgX until its saturation. The amount of supplied CH₃I passed through Tube-1 after the saturation of AgX, therefore the relation between untrapped CH₃I amount and supplied CH₃I amount showed linear relation having Slope 1 as presented in Fig. 7.

The solid lines in Fig. 7 are fitting line for the breaking through experiment results having Slope 1. From the intercept of these fitting lines, the apparent sorption capacity was determined for different amount of AgX in Tube-1.

Figure 8 shows dependence of the apparent sorption capacity at different amount of AgX. As shown in Fig. 8, the apparent sorption capacity increased at first and became constant when more AgX was loaded in Tube-1. Since contact area of AgX for CH₃I was limited when loaded amount of AgX was small, a part of CH₃I was supposed to have passed Tube-1 without contacting with AgX in the range of 2.5 to 5g of AgX. Based on this result, the sorption capacity was determined to be 0.21g / g (AgX) at 24 °C, from the plateau area of plotted data in Fig. 8.

Figure 9 shows the change of the apparent sorption capacity at different CH₃I flux condition. The apparent sorption capacity was unchanged in the range of CH₃I flux from $1.09 \times 10^{-4}$ to $2.33 \times 10^{-4}$g/cm²s. This result indicated that sorption capacity of AgX can be maintained even in high CH₃I flux condition, where high concentration of CH₃I passed through the AgX sorption column in short time. Our result also indicated that the sorption of CH₃I on AgX is kinetically enough for fast reaction under the examined condition.

Figure 10 shows the change of the apparent sorption capacity affected by humidity. When the humidity was increased, the apparent sorption capacity was unchanged from ~0 to 0.01%H₂O, but it decreased from 0.21 to 0.19 g / g (AgX) at 3% H₂O. This result implies that the absorbed water in AgX might occupy sorption site and decreased the sorption capacity of CH₃I.
Humidity in the vent gas seems to be very low. Since the orifice makes vent gas superheated vapor state in the FCVS, so if an effective countermeasure against the condensing into water, AgX seems not to be affected by sorbing humidity.

Figure 11 shows the effect of sorption temperature on the capacity. When the sorption temperature was increased, the apparent sorption capacity increased from 0.21 to 0.61 g / g (AgX) in the temperature range from 24 °C to 170 °C. Higher temperature seems to cause H₂O desorbing from AgX and increase the number of micro cages in AgX which can be used for absorption. As a result, higher temperature increased the apparent sorption capacity of AgX. In the FCVS, AgX is expected to contact with vent gas at 130 ~140 °C. So higher sorption performance should be considered by comparing it with that at normal temperature.

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