INFLUENCES OF IMPURITIES ON IODINE REMOVAL EFFICIENCY OF SILVER ALUMINA ADSORBENT

Tetsuo FUKASAWA*, Kiyomi FUNABASHI*, and Yoshikazu KONDO**

* Power & Industrial Systems R & D Division, Hitachi, Ltd.
7-2-1 Omika, Hitachi, Ibaraki, 319-12 Japan

** Hitachi Works, Hitachi, Ltd.
3-1-1 Saiwai, Hitachi, Ibaraki, 317 Japan

Abstract

Silver impregnated alumina adsorbent (AgA), which was developed for iodine removal from off-gas of nuclear power and reprocessing plants, has been tested laying emphasis on investigation of the influences gaseous impurities have on adsorbent chemical stability and iodine removal efficiency. The influences of the major impurities such as nitrogen oxides and water vapor were checked on the chemical state of impregnated silver compound ($AgNO_3$) and decontamination factor (DF) value.

At 150℃, a forced air flow with 1.5% nitrogen oxide ($NO/NO_2=1/1$) reduced silver nitrate to metallic silver, whereas pure air and air with 1.5% NO_2 had no effect on the chemical state of silver. Metallic silver showed a lower DF value for methyl iodide in pure air (without impurities) than silver nitrate and the lower DF of metallic silver was improved when impurities were added.

At 40℃, a forced air flow with 1.5% nitrogen dioxide (NO_2) increased the AgA weight by about 20%, which was caused by the adsorption of nitric acid solution on the AgA surface. AgA with 10wt% silver showed higher weight increase than that with 24wt% silver which had lower porosity. Adsorption of acid solution lowered the DF value, which would be due to the hindrance of contact between methyl iodide and silver.

The influences of other gaseous impurities were also investigated and AgA showed superior characteristics at high temperatures.

I. Introduction

Uranium and plutonium are important energy sources, and can be utilized more effectively by recycling them in the nuclear fuel cycle. In Japan, the first light water reactor started commercial operation in 1969. Now there are 47 reactors in operation and their total power generation capacity is 38 GW. Reprocessing of spent nuclear fuel is carried out at Tokai Reprocessing Plant

where 812.9 tons of uranium was treated by the end of FY 1994. Commercial reprocessing will start at Rokkasho Plant at the beginning of the next century.

The nuclear energy industry adopts multibarrier protection towards radioactivity exposure for human beings and the environment. In particular, radioactive iodine release to the atmosphere must be surpressed because iodine is volatile and apt to concentrate in the thyroid gland. Therefore nuclear facilities, such as nuclear power plants and reprocessing plants, remove radioactive iodine from their off-gas streams.

Iodine removal methods are generally classified into two types, wet ones which absorb iodine into a solution and dry ones which adsorb iodine onto a solid material.[1-3] Both wet and dry methods must take into account the effects of impurities. For example, wet scrubbing with an alkaline solution absorbs not only iodine, but also various impurities, which sometimes leads to drops in the pH value and iodine absorption capacity of the solution. Impurities also sometimes interfere with the reaction of iodine and solid adsorbent.

The authors have been developing an inorganic adsorbent, silver impregnated alumina (AgA) for about 15 years.[4-14] This adsorbent can be applied to off-gas systems of both nuclear power plants and spent fuel reprocessing plants. The influences of impurities were checked on AgA under the various conditions possible in the above systems. This paper reports experimental results of the investigation which laid emphasis on the changes of chemical stability and iodine removal efficiency of AgA in the presence of gaseous impurities. Iodine removal efficiency was evaluated using adosorption capacity and decontamination factor (DF) which is defined as the iodine concentration at the inlet of the adsorbent column divided by that at the outlet.

II. Off-Gas Systems

The adsorbent AgA is intended for application to the tank vent system for the waste solution of boiling water reactors (BWRs), standby gas treatment system (SGTS) of BWRs, and dissolver off-gas (DOG) system of reprocessing plants. A schematic and conditions of these systems are summarized in Fig. 1 and Table 1. Systems characteristics are as follows. The tank vent filter (adsorbent) removes iodine from the off-gas which contains many contaminants and has a high humidity. The SGTS filter removes iodine over a wide range of concentrations during an accident. The DOG filter removes high concentrations of iodine in the presence of nitrogen oxides. Stability of the adsorbed iodine is an important factor for the DOG system because the main radioactive iodine isotope is I-129 (half life: $1.57 \cdot 10^7$y), whereas I-131 (8.02d) is the main radioisotope for the tank vent system and SGTS. Furthermore, iodine concentration is high (~30ppm) for the DOG, whereas it is below 0.1ppm for power plants (tank vent and SGTS). So two types of AgA were prepared, AgA with 24wt% Ag and 10wt% Ag for DOG and power plants, respectively. Operation temperatures differ for the

three systems. The most severe situation seems to be that of the tank vent because of the low temperature and high humidity. Water vapor clogs the adsorbent pores. Other systems may have low temperature conditions would be exist such as during storage before and after use, and at operation standby. Nitrogen oxides of high concentration also can interfere with the reaction of iodine and impregnated silver, and change the chemical form of impregnated silver. All these factors must be considered in order to apply AgA to actual systems.

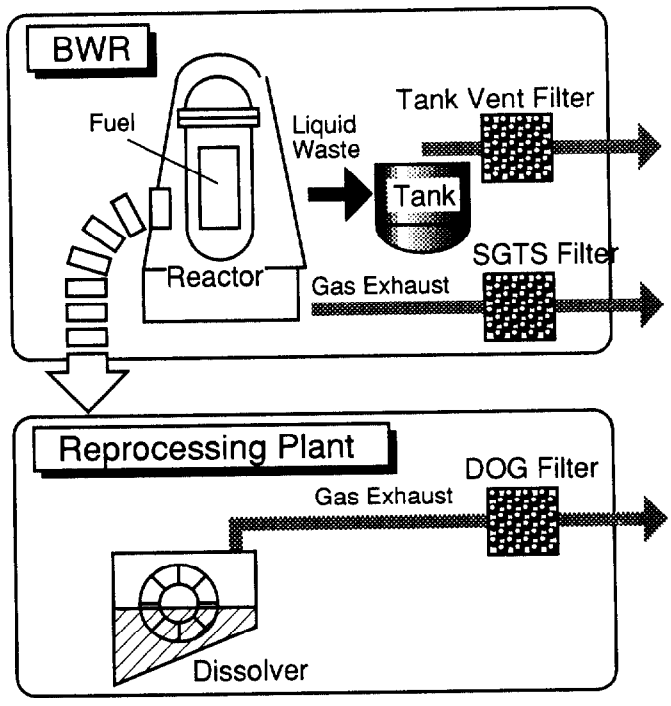

Fig. 1 Off-Gas Treatment Systems

Table 1 Off-Gas Conditions of Each System

System	Off-Gas Conditions				Requirement *filter bed depth
	Temp.	RH	[I]	[NOx]	
(1)Tank Vent Off-Gas → Demister HEPA Iodine HEPA Filter → Stack Waste Tank	30℃	50-90%	1ppb (10^{-3} ppm)	10ppb (10^{-2} ppm)	· High removal efficiency (DF>10 at 5cm*)
(2)SGTS Demister HEPA Iodine HEPA Filter → Stack Reactor Building	66℃	<70%	1ppt–0.1ppm (10^{-6} -10^{-1})	10ppb (10^{-2})	· High removal efficiency (DF>34 at 5cm*)
(3)Dissolver Off-Gas Off-Gas → Mist Filter HEPA Iodine Filter HEPA → Stack Dissolver	150℃	~1%	30ppm	1.5% (1.5×10^{4})	· High removal efficiency (DF>250 at >85cm*) · High adsorption capacity

III. Experimental

The preparation of AgA was described previously.[14] Both types of AgA tested here had particle diameter of about 2mm and pore diameter of from 10 to 100 nm. Specific surface areas of 24 and 10 wt% AgA were about 10 and 40 m^2/g,

and bulk densities were about 1.5 and 1.2 g/cm³, respectively.

The test apparatus is schematically shown in Fig. 2. The iodine species were methyl iodide and molecular iodine. Concentrations of iodine and NOx, ratios of NO to NO_2 of simulated off-gas, the gas temperature and adsorbent bed depth were adjusted to get a desired condition. Iodine concentrations at the inlet and outlet of the column were measured by three methods depending on the form and concentration of iodine, that is gas chromatography with an FID or ECD detector after gas sampling, spectrophotometry using ferric thiocyanate, and inductively coupled plasme mass spectrometry after absorbing the iodine in an alkaline solution.

In order to simulate the standby condition for the DOG system, pre-blow tests were carried out. Pre-blow meant blowing of simulated off-gas without iodine through the AgA column in this study. The weight change of AgA and chemical form of silver were measured during and after pre-blow. The tests of iodine removal were carried out after pre-blow. The breakthrough test was also conducted to confirm the adsorption capacity of AgA with the 10 cm bed depth.

The influences on AgA of other gaseous impurities such as SO_2, NH_3 and CO_2 were investigated with 10 wt% Ag at relatively low temperatures and long times.

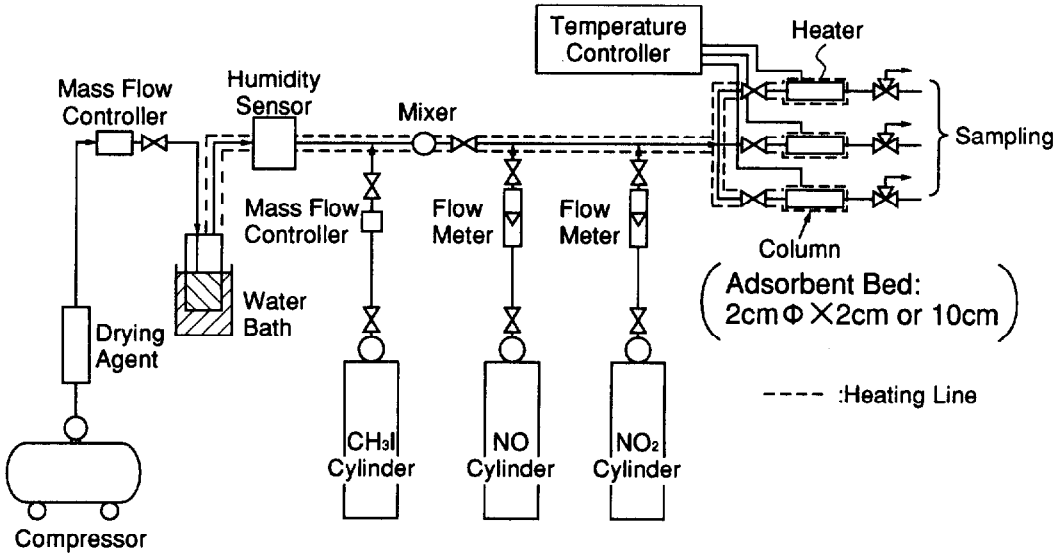

Fig. 2 Outline of the Test Apparatus

IV. Influence of NOx and H_2O on AgA

Before the iodine removal tests, pre-blow tests without iodine were carried out to clarify the influence of only gaseous impurities on the chemical form of impregnated silver. Figure 3 shows the relative weight change of AgA when 1.5% NOx (NO/NO_2=1/1) was blown in at 40 and 150℃. A forced air flow without NOx was carried out as a reference. A slight increase at 40℃ and a decrease at 150℃ were observed in the reference data, which is due to adsorption of H_2O in

the air at 40℃ and desorption of H_2O adsorbed on AgA before the test at 150℃. AgA with 10% silver showed a higher weight increase than AgA with 24% silver at 40℃, which is attributable to the higher surface area of the former. For the NOx pre-blow, weight changes were more notable than the reference case. At 40℃, NOx (NO_2) would be absorbed in the adsorbed H_2O, which would dissolve impregnated $AgNO_3$ and enhance the H_2O adsorption. Nitrate presence which was observed in the 1.5% NO_2 pre-blow supports this mechanism. At 150℃, the weight decrease could not be explained only by the H_2O desorption. In this case, NOx (NO) reduced the impregnated $AgNO_3$ to Ag and decreased the AgA weight. X-ray diffraction (XD) patterns are shown in Fig. 4 for 24% AgA before and after the NOx pre-blow, which indicated the conversion of $AgNO_3$ to Ag by Eq. (1).

$$AgNO_3 + NO \rightarrow Ag + 2NO_2 \quad (1)$$

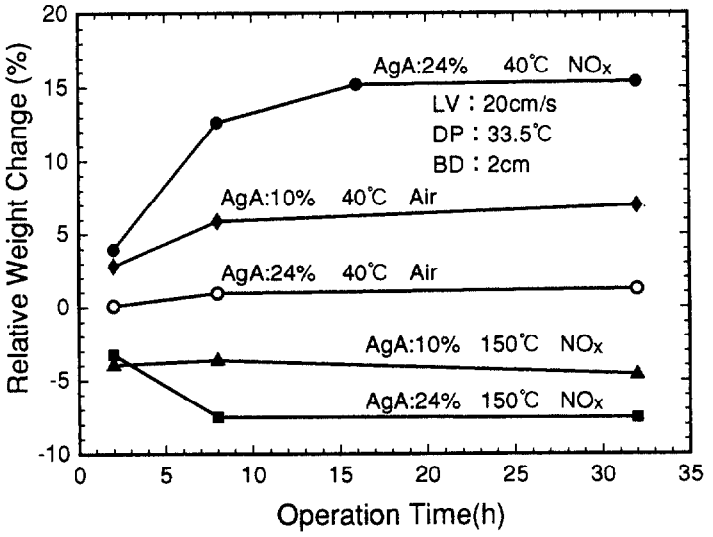

Fig. 3 Relative Weight Change of AgA during NOx Pre-Blow

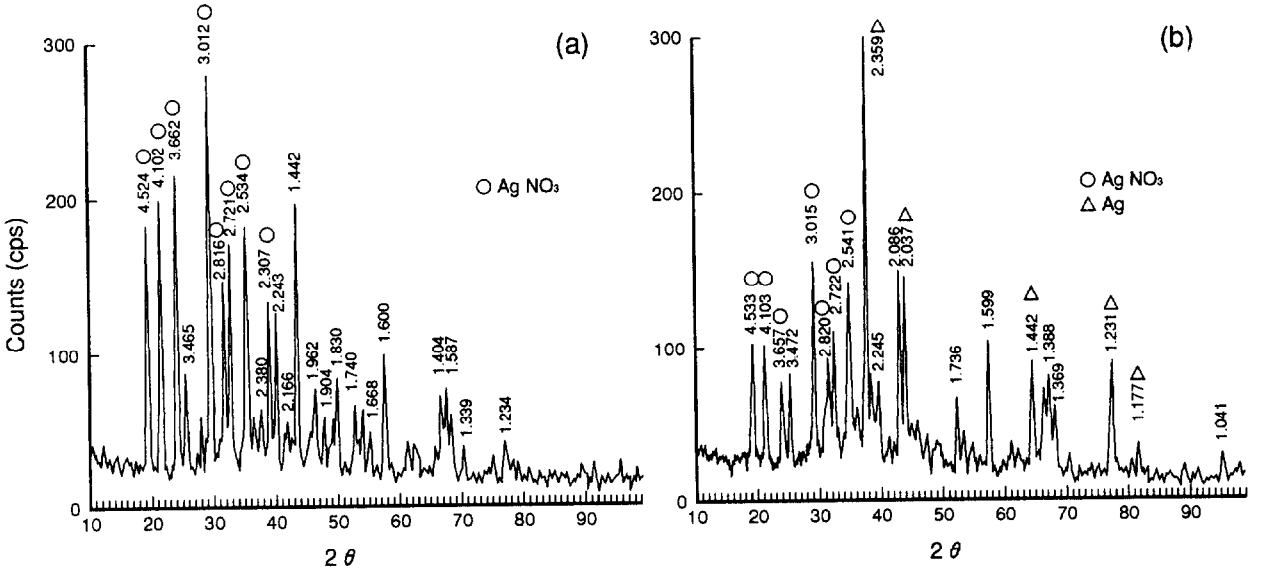

Fig. 4 XD Pattern of AgA before(a) and after(b) NOx Pre-Blow at 150℃

Figure 5 shows the weight change ratio of AgA during the 1.5% NO_2 pre-blow. The data showed that a larger increase was observed for 10% AgA than 24% AgA due to the larger surface area of the former. Compared with the data for 24% AgA in Fig. 3, NO_2 pre-blow had a larger weight increase than NOx pre-blow, which would be due to the easier solution of NO_2 into water than NOx.

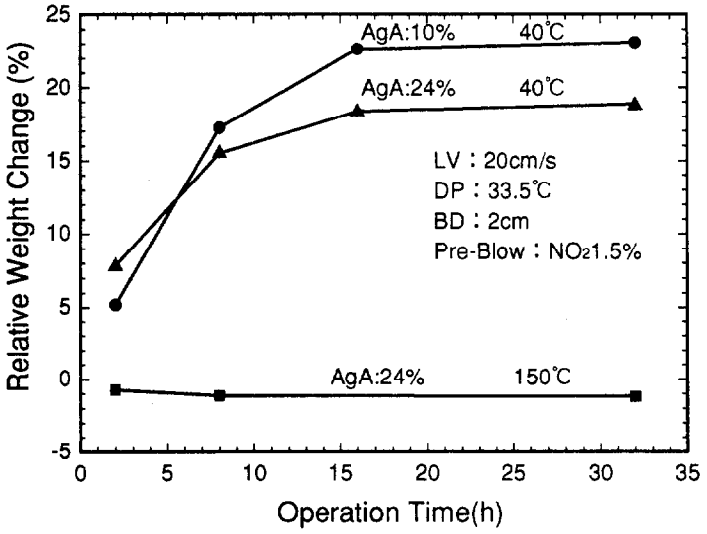

Fig. 5 Relative Weight Change of AgA during NO_2 Pre-Blow

V. Iodine Removal Efficiency after NOx Pre-Blow

Iodine removal experiments were carried out after pre-blow of simulated off-gas without iodine. Iodine was mixed with air without and in same cases with impurities. Typical iodine forms selected here were methyl iodide (CH_3I) and molecular iodine (I_2). CH_3I is the most difficult species to separate from simulated off-gas among the major organic iodines, and I_2 is the main form in the dissolver off-gas of spent fuel reprocessing[1,13]. In the experiments done here, the bed depth was quite small (2cm) to allow sensitive assessment of the change in decontamination factor (DF). It is known that the iodine adsorption band is about 5cm for AgA and a bed depth of 5cm is necessary for good iodine removal. So some cases showed rather rapid iodine breakthrough due only to the insufficient bed depth.

The DF values for CH_3I with 24% AgA are shown in Fig. 6 after various gases were pre-blown as a function of operation time. When the iodine concentration at the column outlet was under the detection limit, a DF value was calculated by substituting the detection limit for the outlet iodine concentration; these values are indicated with an upward pointing arrow in Figs. 6 and 7. The DF value was high after 1.5% NO_2 and air pre-blows. No gaseous impurities were added during the iodine removal test in these two cases. The DF values were low after 1.5% NOx ($NO/NO_2=1$) pre-blow (no NOx during iodine removal), and they

were raised by the addition of NOx during iodine removal. The reactions of CH_3I with silver impregnated on AgA could be written as follows.

$$CH_3I + AgNO_3 \rightarrow AgI + CH_3NO_3 \quad (2)$$

$$CH_3I + Ag \rightarrow AgI + CH_3- \quad (3)$$

$$CH_3I + Ag + NO_2 + 1/2O_2 \rightarrow AgI + CH_3NO_3 \quad (4)$$

Reaction (2) is the normal iodine adsorption reaction which has a high DF. As described in the previous section, NOx pre-blow reduced $AgNO_3$ to Ag. It would be difficult for Reaction (3) to proceed because no couter ions are present for CH_3-, whereas gaseous impurities could act as couter ions as described in Reaction (4).

Figures 7 and 8 show the DF values of 10% AgA after 1.5% NOx and air pre-blows, respectively. Iodine forms of CH_3I and I_2 were examined in both figures. Temperature dependency is summarized in Fig. 8. Molecular iodine (I_2) showed no apparent DF decrease with lower temperature because the reactivity of I_2 with silver would be high. Methyl iodide (CH_3I) showed a lower DF especially at low temperatures and after NOx ($NO/NO_2=1$) pre-blow. This is because of the low reactivity of CH_3I with $AgNO_3$ and the much lower CH_3I reactivity with Ag metal at low temperatures. DF values of over 500 could be obtained for 30ppm CH_3I at 150℃ with 10% AgA in a 2cm bed depth after air pre-blow. AgA with 24% silver showed DF of over 500 even after 1.5% NOx pre-blow.

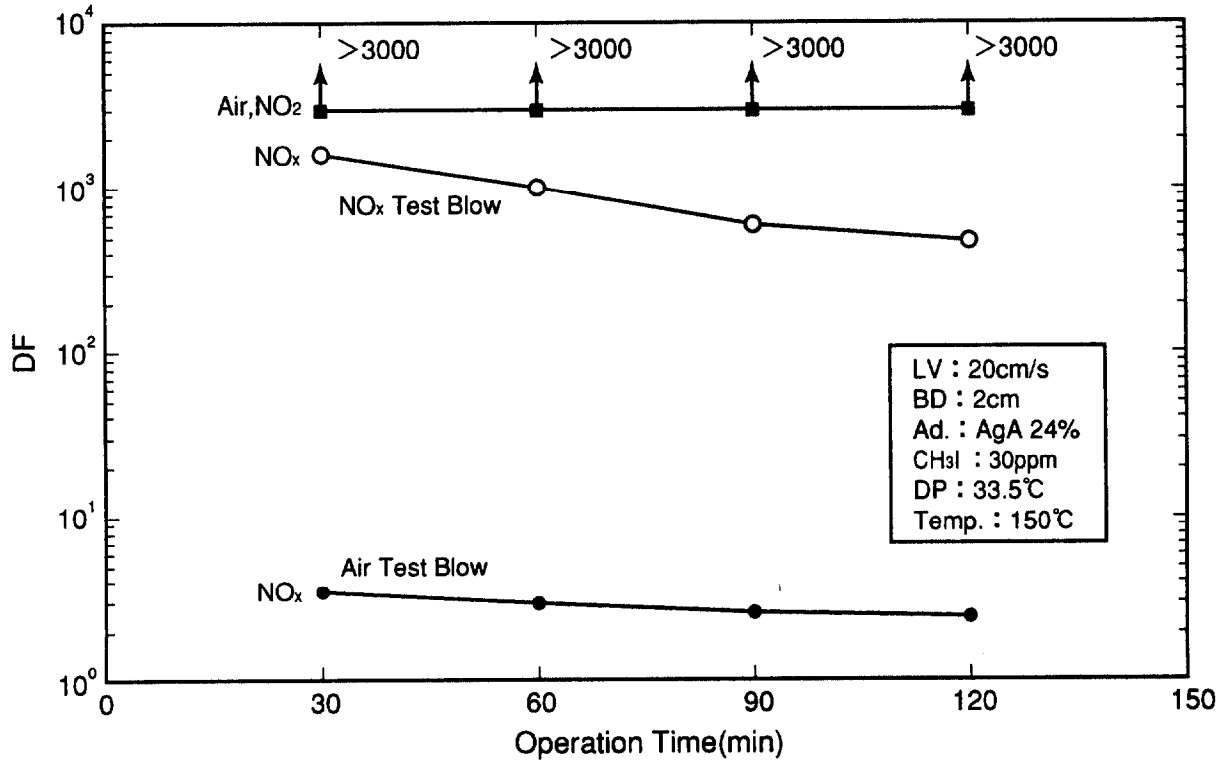

Fig. 6 DF of 24% AgA for CH_3I after Various Gases Were Pre-Blown

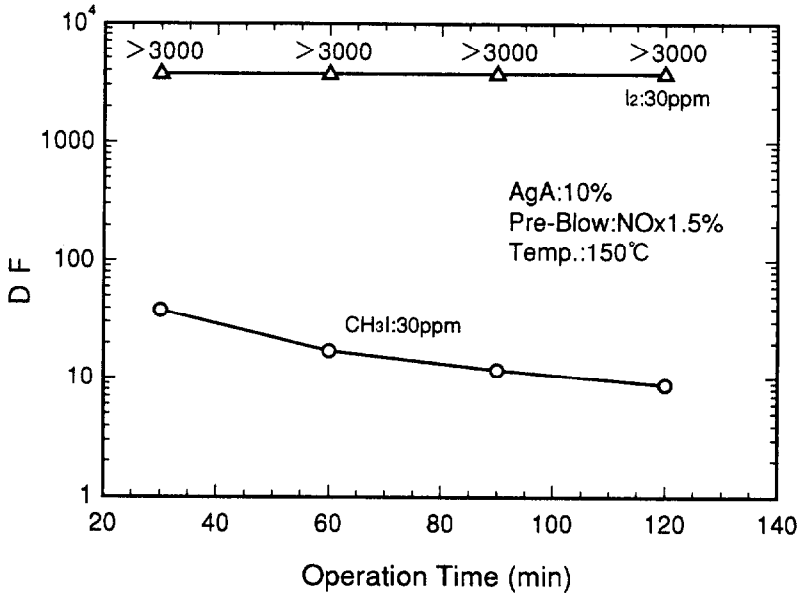

Fig. 7 DF of 10% AgA for CH_3I and I_2 after 1.5% NOx Pre-Blow

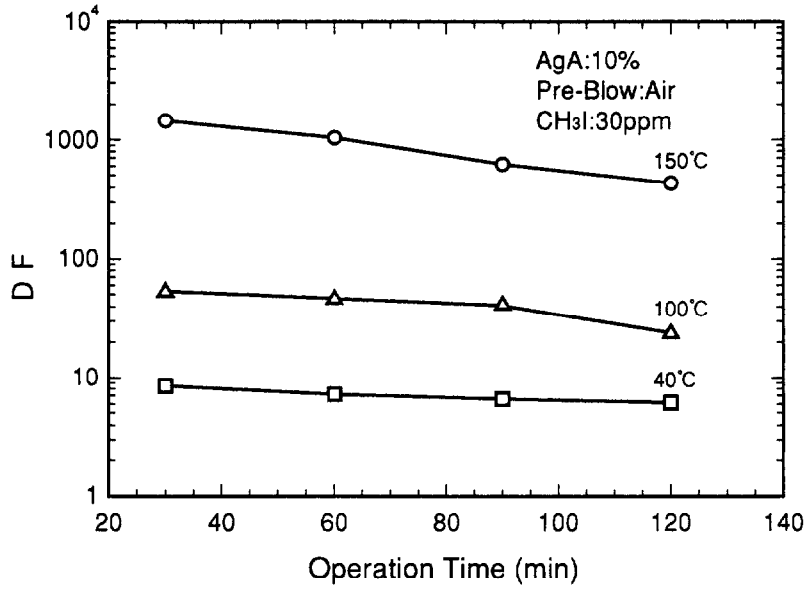

Fig. 8 DF of 10% AgA for CH_3I after Air Pre-Blow

VI. Breakthrough Property of AgA

Iodine breakthrough property was checked in order to get the iodine adsorption capability of AgA in a column. The results are shown in Fig. 9 for AgA with silver contents of 10wt% and 24wt% and CH_3I concentrations of 30 and 300ppm with air blowing. The bed depth of AgA was set at 10cm. Iodine concentration of 300ppm simulated an accelerated condition. AgA is known to show almost the same adsorption capacity for both CH_3I and I_2, and was expected to show a similar breakthrough curve.

The breakthrough point was defined in this study as the operation time

where the DF value decrease was first observed. The breakthrough point depends on the iodine flow rate, and bed volume and silver content of AgA. This could be qualitatively understood by the data in Fig. 9. Iodine adsorption capacity of AgA was about 0.12 g-I/cm³-AgA(10wt%) and 0.35 g-I/cm³-AgA(24wt%). Iodine reacts with the same number of moles of silver in AgA and capacity data obtained indicated about 80% silver utilization. As mentioned before, adsorption band length is around 5cm, so breakthrough point would be full adsorption to 5cm of AgA in this experiment. Calculated breakthrough points of 24% AgA were about 140h and 14h, and those of 10% AgA were about 50h and 5h for 30ppm and 300ppm CH_3I, respectively. Corresponding experimental breakthrough points were 90h, 24h, 48h and 4h, which were not so different from the calculated points. High DF values were obtained for AgA before the breakthrough points which could be predicted by iodine adsorption capacity.

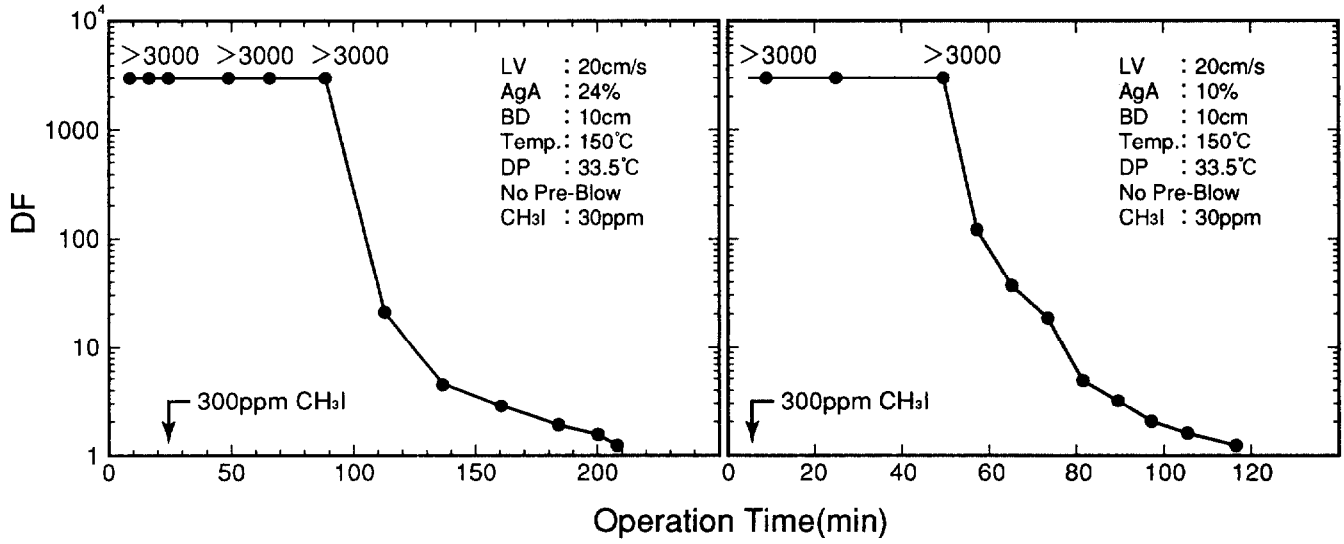

Fig. 9 Iodine Breakthrough Property of AgA

Ⅶ. Long Term Effect of Impurities at Relatively Low Temperatures

In order to check applications to the tank vent and standby gas treatment systems, long term experiments were carried out by blowing simulated off-gas containing various impurities. AgA with 10% silver was exposured for adequate time and iodine was added only at the time of the DF measurement. Impurities were removed from iodine gas to avoid their interference with the DF measurement.

The results are shown in Figs. 10 and 11 for simulated conditions of tank vent and standby systems, respectively. Simulated off-gas of the tank vent system included NOx (5ppb), SO_2 (5ppb), H_2S (<1ppb), HCl (36ppb) and NH_3 (150ppb). Temperature and relative humidity were 30℃ and 70%, respectively. Simulated off-gas of the standby system included NOx (30ppb), SO_2 (<1ppb), H_2S (<1ppb), HCl (<1ppb) and NH_3 (17ppb). Temperature and relative humidity were 66℃ and 70%, respectively. Bed depth of AgA and linear gas velocity were 5cm

and 20cm/s in both cases, respectively. The DF values in Fig. 10 were lower than in Fig. 11 due to the lower temperature for the former. Long term exposures of AgA decreased the DF values in both cases, which would indicate poisoning of AgA by gaseous impurities such as NH_3, NOx and SO_2. The effects of NH_3 and SO_2 were realized by the separate experiments. Nitrogen oxide (NO) reduced $AgNO_3$ to Ag metal and hindered the smooth reaction of CH_3I with silver. The X-ray diffraction pattern showed peaks of Ag metal after exposure to simulated off-gas. But the required DF values were obtained in both cases after long exposure time.

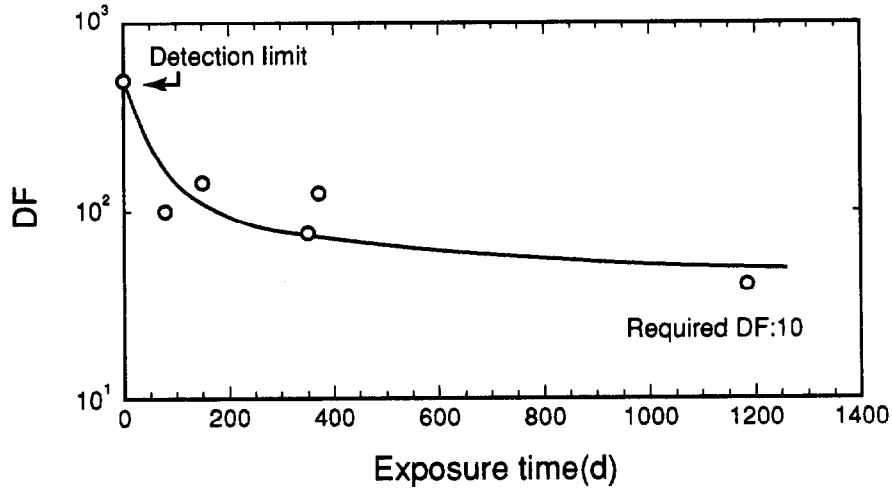

Fig. 10 Long Term DF Change for Simulated Conditions of Tank Vent System

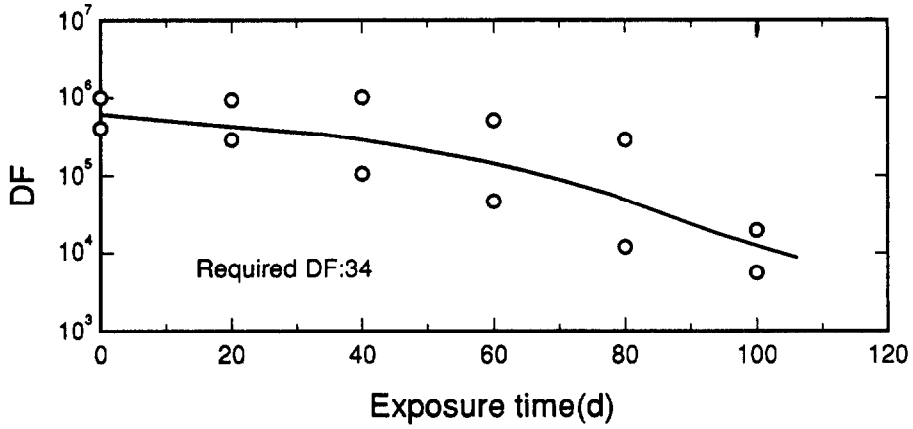

Fig. 11 Long Term DF Change for Simulated Conditions of Standby System

VIII. Conclusions

Silver impregnated alumina adsorbent (AgA), which was developed for iodine removal from off-gas of nuclear power and reprocessing plants, has been tested, placing emphasis on the investigation of influences of gaseous impurities on AgA chemical stability and iodine removal efficiency. Methyl iodide (CH_3I) and molecular iodine (I_2) were chosen as iodine forms for testing. Silver contents

of AgA were 10 and 24 wt%. The main impurities are nitrogen oxides and water vapor in the dissolver off-gas of a reprocessing plant. Their influence on the chemical state of impregnated silver compound ($AgNO_3$) and decontamination factor (DF) value was checked.

At 150℃, air pre-blow with 1.5% nitrogen oxide (NO/NO_2=1/1) reduced silver nitrate to metallic silver, whereas pure air and air with 1.5% NO_2 had no effect on chemical state of silver. Metallic silver showed a lower DF value for methyl iodide in pure air (without impurities) than silver nitrate and the higher DF value in the presence of impurities. These phenomena could be explained by the reactivity difference of methyl iodide with silver in the presence and absence of counter ions (NO_3-, etc.) for methyl ion (CH_3-). Iodine could easily react with silver while methyl ion could react with counter ion. Methyl iodide removal by metallic silver without gaseous impurities could not offer the counter ion for methyl ion and showed a relatively low DF value.

At 40℃, air pre-blow with 1.5% nitrogen dioxide (NO_2) increased the AgA weight by about 20%, which was caused by the adsorption of nitric acid solution on the surface of AgA. AgA with 10wt% silver showed a higher weight increase than that with 24wt% silver which had lower porosity. Adsorption of acid solution lowered the DF value, which would be due to the hindrance of contact between methyl iodide and silver. AgA showed a relatively high DF at high humidity than other iodine adsorbents by keeping high reactivity of dissolved iodine with dissolved silver nitrate, but nitric acid solution would suppress both dissolutions.

The long term influence of other gaseous impurities was also investigated on 10% AgA at 30℃ and 66℃ which simulated the conditions of the tank vent and standby systems, respectively. The impurities of NH_3 and SO_2 decreased the DF value at high humidity. But DF was still over the required value after a long time. AgA indicated superior characteristics at high temperatures.

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DISCUSSION

JUBIN: When you examined the material and determined that you had metallic silver, did you have an opportunity to look at this material through an electron microscope and determine whether the silver was uniformly distributed over the material? Did it, perhaps, conglomerate into nodules of some sort?

FUKASAWA: We did not examine it by microscope in this case, but observed that the silver distribution was under the surface of the other adsorbent. Inside the adsorbent there was still silver nitrate.

HERRMANN: We agree with your experiences that elemental silver has good removal efficiency for iodine. We do not agree with your experience for the removal efficiency of elemental iodine with elemental silver. 85% of I in WAK offgas is organic iodine. With elemental silver on a carrier of silica we found better removal efficiency than with silver nitrate. I agree, we should compare plant and laboratory experiences. Laboratory experiences with I-131 indicate a higher iodine trapping performance than plant experience.

FUKASAWA: I don't know the exact conditions of your offgas, but in these cases the silver nitrate is converted to metallic silver. Without impurities during the iodine separation with metallic silver, this adsorber shows low DF. But with impurities, there should be impurities in the actual offgas, this adsorber showed high DF. So your case is, I think, the same as this case. You get high DF for I_2 with metallic silver with impurities like NO_x or humidity.

HERRMANN: The device for iodine removal is at 140° C. As impurities we have some percent of NO_2. It depends on the dissolution time. We measured it also in the effluent ventilation system where the concentration is much lower. The water content was always approximately 3% absolute, the offgas saturation after the scrubbing columns. This is what we know about the impurities we have.

FUKASAWA: In our case, NO_x concentration is 1.5%. NO is 0.75% and NO_2 is 0.75%. The minimum water content was about 1% in our iodine separation tests. With such an amount of coexisting impurities, you don't have to worry about the DF decrease in this case. In your case you can get high DF I think.

JUBIN: One other question, what is your dew point, is it 35°C?

FUKASAWA: Yes, dew point is 33.5°C at 150°C, humidity is about 1%.