

EVALUATION OF OPTIMAL SILVER AMOUNT FOR THE REMOVAL OF METHYL IODIDE ON SILVER-IMPREGNATED ADSORBENTS

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Abstract

The adsorption characteristics of methyl iodide generated from the simulated off-gas stream on various adsorbents such as silver-impregnated zeolite (AgX), zeocarbon and activated carbon were investigated. An extensive evaluation was made on the optimal silver impregnation amount for the removal of methyl iodide at temperature up to 300°C. The degree of adsorption efficiency of methyl iodide on silver-impregnated adsorbent is strongly dependent of impregnation amount and process temperature. A quantitative comparison of adsorption efficiencies on three adsorbents in a fixed bed was investigated. The influence of temperature, methyl iodide concentration and silver impregnation amount on the adsorption efficiency is closely related to the pore characteristics of adsorbents. It shows that the effective impregnation ratio was about 10wt%, based on the degree of silver utilization for the removal of methyl iodide. The practical applicability of silver-impregnated zeolite for the removal of radioiodine generated from the DUPIC process was consequently proposed.

1. INTRODUCTION

During the irradiation of nuclear fuel in nuclear power plants, various hazardous radionuclides are generated. In connection with the health and environmental impacts, specially, the preventing of the release of these radioactive materials to the environment has become a very important issue in nuclear-waste R&D program. Among these radioactive wastes, it is widely recognized that radioiodines such as elemental iodines (I , I_2), organic iodide (CH_3I) and hypoiodous acid (HOI) are the most important nuclides due to their volatility and the significant radiological effects on the human body and environment [1,2]. Controlling the release of these species depends on the design of the off-gas treatment and ventilation systems within each particular process of nuclear power plant and also on the reactor type.

The removal of radioiodines from the gaseous effluents of nuclear power plant has generally been performed using activated carbon [3–6]. Specifically, the technology for the retention of radioiodine has been improved by the impregnation of activated carbon [3–5]. Tertiary amine-impregnated carbons have been originally developed for the control of various halide-type toxic gases to form the stable quaternary salts on the surface of activated carbon [5]. Their use to control the organic radioactive halides, especially CH_3I , has been introduced by Collins et al. [6]. Among these halide complexing amines, TEDA (TriEthylene DiAmine) is widely used in the world for nuclear facility air cleaning [4].

During the past several decades, carbon adsorbents, such as KI-impregnated and TEDA-impregnated activated carbons have been widely studied. Although activated carbon has been successfully used in power plant, activated carbon cannot be considered as a primary sorbents at high temperature systems, because of its low ignition temperature and its adverse reaction with nitrogen oxide [5]. These factors virtually rule out the use of this material at high temperature systems like DUPIC (Direct Use of Spent PWR Fuel In CANDU Reactor) process. As a result, the promising approach to the problem of iodine removal under high temperature conditions is to use of inorganic adsorbents in which a stable iodine compound is formed. Numerous studies for the removal of radioiodine from off-gas stream of nuclear facilities have been performed with various silver-impregnated inorganic adsorbents [7–11]. These systems in which adsorbents function as primary

filtering of radioiodine have some advantages in their simplicity and smaller amounts of secondary radioactive wastes in comparing with wet processes. Although a number of studies have been conducted to evaluate the loading of both elemental and methyl iodide on silver impregnated zeolite (AgX), these studies focused primarily on the macro-scale (deep-bed) during evaluating the material under a broad range of process conditions and contaminants for total bed loading at the time of breakthrough. A few studies have evaluated the equilibrium and maximum loading capacities of the AgX [7–13]. In our laboratory, preliminary performance tests for the removal of methyl iodide by various silver-impregnated adsorbents had already been carried out [14]. However, more detailed studies are needed to establish a silver utilization for the removal of radioiodine as a function of process temperature.

The purpose of this study is to evaluate the characteristics of gaseous methyl iodide trapping on the base adsorbents including AgX. In this approach, the influence of impurities such as water vapor or nitrous oxide was not considered. The comparison of loading capacities on various adsorbents was carried out in a fixed bed, based on the saturation of adsorption capacity in all experimental tests. Major parameters affecting adsorption behaviors are temperature, input concentration of methyl iodide, and silver impregnated ratio. From the standpoint of silver utilization for the removal of methyl iodide both the optimal operating temperature and the effective silver impregnated ratio were determined.

2. EXPERIMENTAL

2.1. Materials

The sodium form zeolite (NaX) of 8~16 mesh of Linde Molecular Sieves 13X(Supplied by Aldrich Co., USA) was used to prepare a silver-impregnated zeolite, AgX. As a preliminary experiment to compare the adsorption capacity of other adsorbents, zeocarbon(ZC) of 2~3 mm sphere (ZEObUILDER Co., KOREA) and activated carbon of 8~16 mesh granule (Supplied by SAM CHUL RI Co.,KOREA) were also selected. Zeocarbon is composed of activated carbon (40 wt%) and zeolite 5A (60 wt%). Table 1 shows the physical properties of various base adsorbents used for methyl iodide removal.

TABLE 1. PHYSICAL PROPERTIES OF VARIOUS BASE ADSORBENTS

Adsorbents	MS-13X	Zeocarbon	Activated Carbon
Average Pore Diameter, Å	24.5	26.6	10
Surface Area, m ² /kg,	7.99 × 10 ⁵	5.29 × 10 ⁵	1.437 × 10 ⁶
Total Pore Volume, m ³ /kg	3.56 × 10 ⁻⁴	3.82 × 10 ⁻⁴	7.67 × 10 ⁻⁴
Micropore Volume, m ³ /kg	2.37 × 10 ⁻⁴	2.15 × 10 ⁻⁴	4.25 × 10 ⁻⁴

2.2. Impregnation (or ion exchange) technique

The silver-impregnation of zeolite was prepared through ion exchange in a batch reactor. Prior to water exposure, NaX was purged with a water-saturated air stream at room temperature for three days to equilibrate it with moisture. This prevents bead fissure of the NaX on soaking in water. Zeolite was washed with distilled water to remove fines. The NaX stirred with magnetic bar in the beaker was exchanged with silver nitrite (AgNO₃) for 8 hours at room temperature. After an ion exchange, AgX was washed with distilled water to remove the excess salt ions. The AgX was dried to a constant weight in a vacuum oven at 150°C for 24 hours. Then, silver-impregnation amount of each AgX was obtained by weight gains from initial weight of 13X. The physical properties of AgX measured by BET-N₂ analysis are listed in Table II.

TABLE II. PHYSICAL PROPERTIES of SILVER IMPREGNATED ZEOLITE

Adsorbents	NaX (13X)	AgX (10wt%)	AgX (20wt%)	AgX (30wt%)
Pore Size, Å	24.5	24.4	23.4	23.6
Surface Area, m ² /kg	7.99×10^5	7.95×10^5	7.2×10^5	6.99×10^5
Total Pore Volume, m ³ /kg	3.56×10^{-4}	3.22×10^{-4}	2.88×10^{-4}	2.81×10^{-4}
Micropore Volume, m ³ /kg	2.37×10^{-4}	2.05×10^{-4}	1.92×10^{-4}	1.83×10^{-4}

2.3. Adsorption/desorption experiments

The schematic diagram of experimental apparatus was shown in Fig. 1. The vapors of methyl iodide are produced from an evaporation of aqueous methyl iodide. Gas-phase concentration is adjusted by controlling the liquid temperature and the nitrogen flow rate to methyl iodide generators. Dry air was used as a carrier gas at 4 l/min, linear velocity of 0.26 m/sec. All parts of the system, the adsorption column, mixing baffle and gas flow lines, were made of glass and pyrex to prevent the elemental iodine plate-out and methyl iodide trapping. Temperature of the adsorption column (0.018 m I.D. × 0.6 m Length) was changed up to 300°C by heating electric furnace. Constant amount of adsorbents is packed in an adsorption bed. The gaseous methyl iodide enters to column packed with constant amount of adsorbent. The methyl iodide concentration from the effluent was analyzed by the gas chromatography with a pulse discharged detector (PDD) and GS-Q capillary column at oven temperature of 140°C.

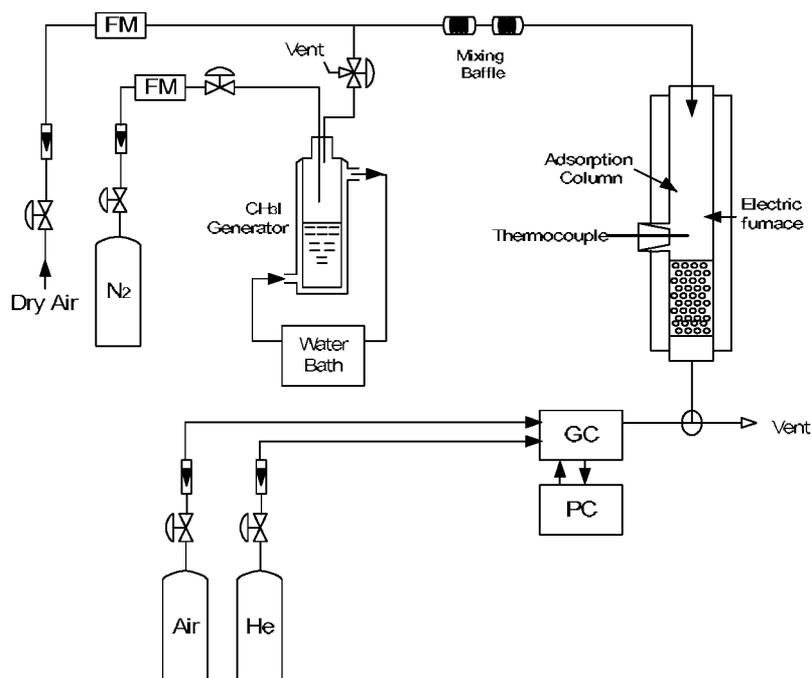


FIG. 1. Schematic diagram of methyl iodide adsorption under a high temperature condition.

3. RESULTS AND DISCUSSION

In order to compare the adsorption capacities of methyl iodide on three kinds of base adsorbents, such as activated carbon, zeocarbon and 13X, preliminary tests were carried out at constant test conditions, stated in experimental section. Fig. 2 showed the variation of adsorption amounts of methyl iodide for three base materials at a temperature range of 30°C to 300°C. It indicates that the activated carbon has an excellent adsorption capacity at 30°C compared to the others. The adsorption capacity, however, of activated carbon markedly decreases as the temperature increases. On the other hand, 13X showed the higher adsorption capacity of methyl iodide as the temperature increases. Zeocarbon shows a similar adsorption pattern of activated carbon at higher temperature range. It implies that synergy effect due to the mixing of two materials has not appeared in adsorption capacity. Low adsorption capacities on both activated carbon and zeocarbon at high temperature would be caused by higher desorption rate than adsorption rate. As reported in previous investigation [15], this result would be another evidence that activated carbon has poor methyl iodide retention at a high temperature range compared to zeolite 13X. The increase in the adsorption capacity of methyl iodide on 13X at a higher temperature up to 300°C is due to both physisorption and chemisorption occurred in the zeolite matrix.

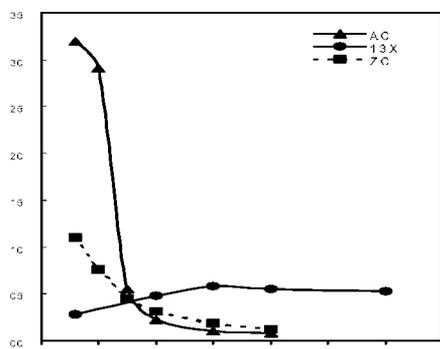


FIG. 2. Adsorption amounts of methyl iodide on various base adsorbents as a function of temperature.

Adsorption capacities of methyl iodide on the various AgX were evaluated as a function of a temperature and the amount of silver impregnation. Tests were conducted to determine the maximum adsorption capacities of 13X and three types of AgX, such as 10, 20 and 30 wt%. Variations between adsorbed amounts and desorbed amounts of methyl iodide are shown in Fig. 3 and 4, respectively. As shown in Fig. 3, the adsorption capacity of methyl iodide on each AgX showed the maximum value in the temperature range of 150°C to 200°C. It would be convinced that the optimal temperature for removal of methyl iodide by AgX is about 200°C. The decrease in adsorption amounts at 300°C may be due to the higher desorption rate than the adsorption rate including chemical reaction between silver and methyl iodide. It is observed that a high silver impregnation amount is attributed to an increase of adsorption capacity of methyl iodide. The adsorption amount of methyl iodide, however, is not proportional to their silver amounts. This result would be inferred that all impregnated silver in the matrix would not chemically react with the methyl iodide as silver amount increases. It seems that a higher silver impregnation would cause the partial blocking of the adsorption sites to increase the portion of the unreacted silver in the matrix.

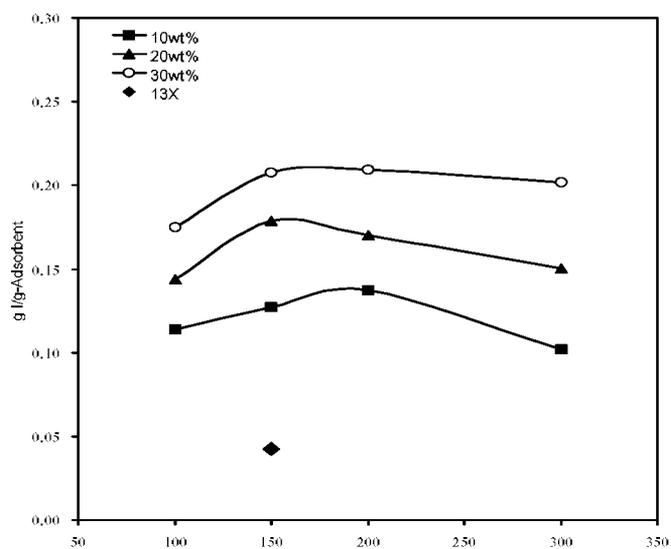


FIG. 3. Adsorption amounts of methyl iodide on 13X and various AgX as a function of temperature (Weight = 7.05g, Input conc. = 2.5×10^{-5} mol/l).

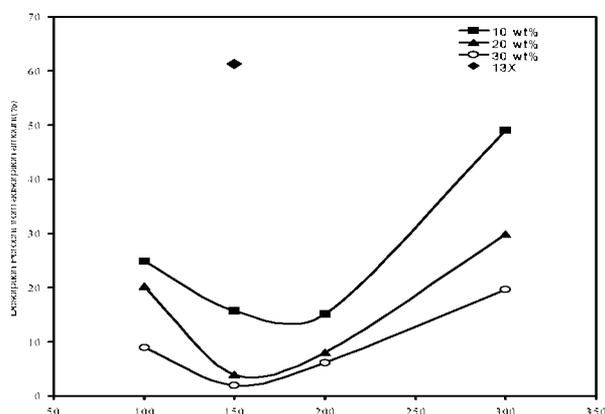


FIG. 4. Desorption percent of methyl iodide on 13X and various AgX as a function of desorption temperature.

According to the previous studies [10, 13], elemental iodine and methyl iodide has a kinetic diameter of $\sim 5 \text{ \AA}$ and $\sim 6 \text{ \AA}$, respectively. In general, the average pore size of 13X is $\sim 12 \text{ \AA}$ in radius. The effective pore sizes could be slightly changed by substituting Ag^+ for Na^+ . As indicated in Table 1, the reduction in a total pore volume of AgX, especially micropore volume seems to be almost proportional to the impregnated silver amount. However, the decrease in surface area of AgX with 10 wt% is not so great compared to other AgX sorbents. It was also reported that no silver nodules on AgX or AgZ were detected [10]. As a result, partial blocking of micropore due to Ag impregnation forms AgX sites which methyl iodide molecules hardly diffuse into.

As mentioned earlier, the relatively high silver impregnation shows the increase of unreacted portion of silver in methyl iodide adsorption. The adsorption capacity at a given silver impregnation amount showed the maximum value in a range of $150^\circ\text{C} \sim 200^\circ\text{C}$. Based on a stoichiometric chemical reaction between methyl iodide and silver, the silver utilization attributed to the removal of methyl iodide depends on the silver amount impregnated in a zeolite matrix. As shown in Fig. 5, the highest silver utilization percent of $\sim 85\%$ was obtained at the 10 wt% of AgX. It indicates that maximum theoretical loading on AgZ (or AgX) is 237 mg $\text{I}_2/\text{g-adsorbent}$ [10, 12].

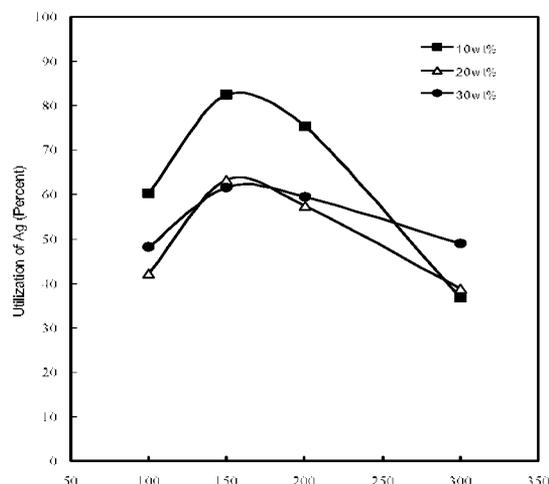
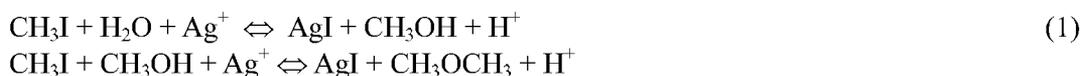
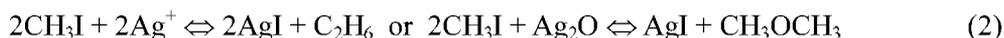


FIG. 5. Utilization percent of silver for the removal of methyl iodide on various silver impregnated zeolite based on the chemical reaction.

The previous studies reported the reaction between methyl iodide and silver on AgZ as following equation [10, 12, 13]:



However, the exact mechanism of reaction between methyl iodide and AgX has not yet been reported. Therefore, in order to identify this mechanism, some experiments to analyze the following reaction under the absence of water vapor will be performed.



4. CONCLUSIONS

Removal capacity of methyl iodide on various silver impregnated zeolites (AgX) was evaluated as a function of temperature and silver impregnated amount. As the result of preliminary test, zeolite 13X as a base adsorbent showed the good performance in removal of methyl iodide at a high temperature up to 300°C compared to the activated carbon and zeocarbon. The maximum adsorption capacity of AgX was observed at the range of 150 to 200°C. The adsorption capacity of AgX increases when the silver amount becomes higher. However, it was found that the 10 wt% of AgX as an optimal silver-impregnation ratio resulted in silver utilization of about 85% for the effective removal of methyl iodide at 150°C.

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