DEVELOPMENT OF ORGANIC IODINE ADSORBENTS

J.F. WANG, T. KOBAYASHI, Y. UZUYAMA
Advanced Microelectronics Materials Development Centre, Rasa Industries, Ltd, Japan
26-2, Otonashi, Aza-Yamazaki, Sanbongi, Osaki-Shi, Miyagi 989-6313, Japan

K. ENDO
Electronic Material Department, Rasa Industries, Ltd, Japan
Yaesu Dai Bldg., 1-1-1, Kyobashi, Chuo-Ku, Tokyo 104-0031, Japan

ABSTRACT

High-efficiency adsorbents for organic iodine removal, silver-exchanged zeolites (Rasa-AgX and -AgR), have been developed and their adsorption characteristics have been investigated. The results show that AgX and AgR have the very high adsorption efficiencies of organic iodine. In particular, they also show excellent adsorption performances in the environment of the existence of hydrogen and the steam condensation. The long-term storage experiments have been gone on for two years for AgX and one year for AgR. Till now, their deterioration in adsorption efficiency is not observed at all. The experimental results of water immersion and heat-treatment at high humidity show that AgX and AgR are very stable. Owing to above reliable results, AgX is being used at Japanese nuclear power plants as their countermeasures of severe accident. At present, more facilities are considering adopting these filters in their venting systems.

1. Introduction

In a severe accident, the most important task is to prevent radioactive materials from having an impact on the environment for a nuclear facility. In the process of nuclear fuel irradiation at nuclear power plants (NPPs), specially, when a severe nuclear accident happens, some hazardous radionuclides will be generated. These radionuclides include noble gases, aerosols and iodine. Noble gases like Xe can be removed by a hold-up system. Particulate aerosols such as Cs, Te and Sr can be removed by the high-efficiency particulate air (HEPA) filters, metal filters and alkaline scrubbers. As for the radioactive iodine, its removal has different situation from above those substances. Radioactive iodine has two forms. One is elemental iodine (I_2, I), and another is organic iodine (CH_3I). The former can be easily removed by a wet scrubber, and the latter is difficult because it is highly diffusible in air and insoluble in water.

Radioactive iodine is very harmful to our health because of its strong toxicity. If people are in radioactive iodine environment, their body will be contaminated by inhalation pathway in a few minutes. The inhaled radioactive iodine will incorporate with the body and immediately migrate to the thyroid [1, 2]. Numerous study results have showed that people who exposed to radioactive iodine will increase risk of cancer compared to those who did not.

A filtered containment venting system (FCVS) at NPPs is commonly used to remove radioactive iodine. In FCVS, an adsorbent plays an important role. Hence, in recent years much attention has been paid to investigate high-performance adsorbent. Up to the present, several solid adsorbents have been developed. KI and TEDA (triethylene di-amine) impregnated activated carbon as the successful examples are being applied to facilities including NPPs [3]. However, these filters cannot be used at high temperature environment due to their low ignition temperature. Furthermore, they also require an external power supply to maintain the effectiveness in a high humidity environment. Once the power supply shuts down, these filters will loss the filtration function. This fault likely results in the leakage of radioactive iodine to the atmosphere. In order to overcome these shortcomings, the new adsorbents are necessary. Otherwise, as different nuclear facilities have different venting conditions, the adsorbents matched with these conditions are demanded.

In order to satisfy these requirements, the new organic iodine adsorbents, Rasa-AgX and -AgR, have been developed based on a large number of experiments [4-6]. The purpose of this paper is to introduce recent evaluation results of AgX and AgR and to summarize their applications to nuclear facilities.

2. Experimental and results

In the earlier some papers [4-6], we described the development process of Rasa-AgX and –AgR as the adsorbents of radioactive iodine by selecting suitable type zeolite and optimizing the production process. Their adsorption characteristics were evaluated under the various conditions including high temperature, high pressure, high relative humidity, variable gas compositions. In order to broaden their application scope, the adsorption characteristics of organic iodine on AgX/AgR in hydrogen atmosphere and at low-temperature have been evaluated, and their stabilities in water and at high temperature have been also investigated.

2.1 Behaviours in hydrogen of AgX and AgR

It is well known that the off-gas from a containment vessel is composed of hydrogen, nitrogen, steam and so on. When hydrogen concentration exceeds 4 vol%, explosion will likely occurred. Therefore, to timely reduction of hydrogen concentration is important. For this reason, the behaviours of AgX and AgR in the atmosphere containing hydrogen were examined.

Table 1 shows hydrogen concentration variation before and after the gas mixture of air and hydrogen flows through AgX. The gases conditions are shown in Table 1. Comparing the hydrogen concentration between inlet and outlet, the reduction of hydrogen concentration can be confirmed. This shows that AgX plays a role in decreasing hydrogen content. As the result, the temperature of AgX slightly increased. This effect of removing hydrogen is very significant in reducing the risk of explosion in a severe accident.

Table 1 Hydrogen concentration before and after the mixed gas (air + H_2) flows through AgX.

Air + H_2 conditions				Initial temp. of AgX(ºC)	Results	
Humid air* flow (ml/min.)	H_2 flow (ml/min.)	Residence time (sec.)	Inlet content of H_2 (%)		Rising of temp. (ºC)	Outlet content of H_2 (%)
6600	205	0.87	3.0	75	1	> 1.5
				120	15	< 0.5
				136	17	< 0.5

*Humid air is generated by bubbling water at room temperature.

Table 2 Adsorption efficiencies of CH_3I on AgR over different periods and gas compositions. Temperature of input gas mixtures was 120 °C; residence time 0.15 second, and DPD 37 K.

Time (min.)	AgR temperature (°C)	Gas composition (Vol.%)	Adsorption efficiency* (%)
0-2	26-122	Steam: 53 % Air: 24 % H_2: 10 % N_2: 13 %	99.9
7-9	101-105		> 99.9
15-17	126		> 99.9
30-32	124		> 99.9
60-62	120		> 99.9

* Detection limit.

In order to examine the effectiveness of AgR in hydrogen atmosphere, superheated steam together with different compositional gases containing hydrogen suddenly flows through AgR adsorbent. This operation creates an environment like initial venting stage in an FCVS. The gas compositions are assumed to be coexistent mixture gases of hydrogen, nitrogen and steam. Table 2 shows adsorption efficiency of CH_3I over different periods. These evaluations were performed by Rasa Industries. Although the steam condensation will immediately occur when the venting valve is opened due to temperature difference between off-gas stream and AgR adsorbent, AgR still shows the high adsorption efficiency of over 99.9%. Here it is emphasized that AgR can safely work in a hydrogen concentration of 10 vol%. This should attribute to the suitable Ag ion concentration and position in crystal structure.

Since AgX and AgR show different behaviours in hydrogen atmosphere, they can be used in different type nuclear reactors with different venting conditions.

2.2 Adsorption characteristics of CH_3I on AgX at the outdoor temperature

According to the description in paper [5], AgX manifests a feature that it has good adsorption characteristics of organic iodine even at high humidity and near room temperature (Table 3). The conditions in Table 3 are thought to be similar to those of a standby gas treatment system (SGTS) in boiling water reactors (BWRs) and an annulus in pressurized water reactors (PWRs). These evaluations were performed by NUCON International Inc. According to the results in Table 3, AgX as an organic iodine adsorbent exhibits a very excellent adsorption performance. Especially, AgX has a proximally 99% adsorption efficiency even if the temperature is near room temperature. These results demonstrate the applicability of AgX to SGTS and annulus.

Table 3 Absorption efficiencies of CH_3I on AgX at different temperatures and relative humidity. Test was performed with system pressure of 103 kPa, linear velocity of 20.3 cm/sec. and concentration of organic iodine (CH_3I) of 1.75 mg/m^3 (I-131).

Bed depth (mm)	Res. time (sec.)	Absorption efficiency of CH_3I (%)			
		RH 95%			RH 70%
		30 ºC	60 ºC	90 ºC	66 ºC
50.8	0.250	98.738	99.685	99.970	> 99.999
76.2	0.375	99.850	99.950	99.983	> 99.999
101.6	0.500	99.962	99.987	99.995	> 99.999

On the other hand, AgX is expected to maintain its high adsorption efficiency in the freezing temperature range because it is hoped to serve an air cleaning filter. For this purpose, AgX was evaluated at lower temperature. As a typical example, adsorption efficiency of CH_3I was evaluated at minus 5 degree. The dew point of atmosphere is from -7 °C to -10 °C, and water content is 0.30 vol% when dew point is -8 °C. In measurement of adsorption efficiency, residence time was 0.61 second, and CH_3I concentration 19.8 ppm. When the AgX temperature decreases to -5 °C, CH_3I was introduced. Then, adsorption efficiency of CH_3I on AgX was measured at different elapsed time. Table 4 shows the measured results. It is evident that AgX still indicates the high adsorption efficiency of at least 99.7% in examined elapsed time range. Summarizing the results in Table 3 and 4, AgX demonstrates excellent adsorption performance for organic iodine in a wide temperature range.

Table 4 Adsorption efficiency of CH_3I on AgX at different elaped time at minus 5°C.

Elapsed time after introducing CH_3I (min.)	Adsorption efficiency (%)
5	99.7
20	99.8
40	99.9
60	99.8
90	> 99.9

2.3 Stability experiments of AgX and AgR

As the products, they must be stable in various environments including high temperature, high humidity, even in water. These stabilities of AgX and AgR have been examined.

2.3.1 long-term storage experiment

In order to investigate the deterioration of adsorption characteristics of AgX and AgR in high humidity environment, they are stored in a closed container filled with water at the bottom of the container shown in Fig. 1. The relative humidity in the container is maintained at 100%. This container is placed at a dark place without air-conditioner, and its temperature variation is consistent with outdoor temperature. The variation range of temperature is 2-30 ^{o}C. Table 5 shows variation of water content, bead hardness and adsorption efficiency for CH_3I of initial and stored samples. According to Table 5, water content in AgX beads increases after AgX was stored over 1.0 year. This is reasonable because the storage container has a higher relative humidity than that of natural environment. Hardness of beads shows slight decrease. This is perhaps related to the immersion of water molecules into the binder. The further experiment will be done for clarifying the mechanism of hardness deterioration. On the other hand, the adsorption efficiency of CH_3I does not change at all for initial and after stored samples in spite of the increase of water content and decrease of hardness. These evaluation results suggest that AgX is stable in adsorption characteristics at high humidity and outdoor temperature. The same experiment for AgR is being also carried out. Up to the present (>1.0 years), no aging in adsorption efficiency is observed.

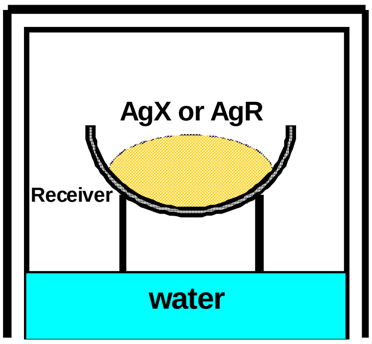

Fig. 1 Schematic diagram of AgX and AgR storage.

Table 5 Adsorption efficiencies of CH_3I on AgX that is stored for different periods. Evaluation conditions: Gas composition: steam100%; Residence time: 0.20 sec.

Storage period	Water content (%)	Hardness (N /bead)	Adsorption efficiency (%)	
			105°C DPD:5K	115°C DPD:15K
Initial	9.4	6.6	>99.95	>99.95
After 1.0 year	17.3	5.2	>99.95	>99.95
After 1.5years	16.0	5.2	>99.95	>99.95
After 2.0years	18.3	5.3	>99.95	>99.95

2.3.2 Heat-treatment experiment

Off-gas stream from an FCVS in BWR or PWR has some features such as high temperature, high humidity, high pressure, large flow and coexistence of hydrogen. Especially, at the beginning of venting, steam condensation will occur due to the temperature difference between off-gas stream and adsorbent. Worryingly, steam condensation has an effect on adsorption performance of an adsorbent. Therefore, it is necessary to examine the thermal stability in high-temperature steam. For this purpose, AgR was heated to 145 ^{o}C in environment humidity of 100%. After different steam-treatment durations, the adsorption efficiency of CH_3I was measured. Table 6 shows measured results at DPDs of 5K and 15K. All results in Table 6 show that the adsorption efficiencies of organic iodine are over 99.9%. These results prove that adsorption performance of AgR does not deteriorate after steam treatment at high temperature.

Table 6 Adsorption efficiency of CH_3I on AgR after steam treatment for different duration. Steam treatment was performed in 100% steam at 145 °C.

Time of steam treatment	Adsorption efficiency of CH_3I	
	105 °C (DPD 5K)	115°C (DPD 15K)
14 days	99.9 %	> 99.9 %
50 days	99.9 %	> 99.9 %
70 days	99.9 %	> 99.9 %
100 days	99.9 %	> 99.9 %

Table 7 shows adsorption efficiency of CH_3I before and after AgR was heat-treated. The heat treatment was performed in air at 450 ^{o}C for 5 days. At the DPD of 5 K, the

Table 7 Comparison of adsorption efficiency of CH_3I on AgR before and after heat treatment. The heat treatment was carried out in air at 450 °C for 5 days.

	Adsorption efficiency of CH_3I	
	105°C (DPD 5K)	115°C (DPD15K)
Before	99.9 %	> 99.9 %
After	99.5 %	> 99.9 %

adsorption efficiency seems to have a slight decrease for heat-treated sample. But when DPD increases to 15 K, the adsorption efficiency recovers to the same value as the before heat-treatment. These results show that AgR is stable even if it was heat-treated at high temperature.

2.3.3 Water immersion experiment

In order to confirm the stability of AgR in water, water immersion experiment was carried out. Put AgX beads 392g (355g in dry base) into 500 ml water (Fig. 2). Immersion water has a room temperature. The immersion was kept for over 16 hours. Then, dry these AgX beads and measure their adsorption efficiency of CH_3I. The results in Table 8 show that the high adsorption efficiencies can be still obtained. On the other hand, elution percentage of Ag ions is below 0.09%. These results exhibit that AgX is stable in water. Above results corroborate that AgX is capable of acting as an organic iodine absorbent even if rupture disk exists and steam condensation occurs during the venting for the first/second time or standby situation.

Fig. 2 AgX beads in water.

Table 8 Adsorption efficiencies of CH_3I on AgX at various temperatures / DPDs. Gas composition is 100% steam. Residence time is 0.19 sec.

Temperature (DPD)	Adsorption efficiency	
	Before immersion	After immersion
107 ºC (7 K)	> 99.9%	> 99.9%
116 ºC (16 K)	> 99.9%	> 99.9%

3. Applications of AgX and AgR

Traditionally, the generation amount of organic iodine is estimated only 0.15% in total radioactive emission when a severe accident happens. Therefore, it is not paid more attention until now. But the recent research reports show that the concentration of organic iodine exceeds the predicted value. In particular, according to the assumption of US Nuclear Regulatory commission [7], 4% iodine released from a reactor will react with organic matter in containment vessel to form 1.3kg methyl iodide when a severe accident happens. In order to take effective measures to prevent the leakage of organic iodine, Japanese electric companies have decided to improve or install the FCVS at all nuclear power plants. There are two main kinds of venting systems. One is WET system, and another is DRY system. However, as mentioned above, these conventional venting systems cannot remove organic iodine effectively. On the other hand, although the doped activated carbon filters are being used in some nuclear facilities, their operating conditions limit the application scope.

AgX and AgR have been proved to be high efficient solid adsorbents under the various harsh conditions. The filters made from AgX or AgR do not need power supply to maintain their effectiveness. These filters can not only remove organic iodine completely, but also they show a good behaviour in hydrogen atmosphere. Moreover, AgX can work in a wide temperature range and AgR in high hydrogen content. Due to these advantages, Tokyo Electric Power Company (TEPCO) is using our AgX filters in its WET system as the countermeasure of organic iodine. The test results from TEPCO demonstrated that the decontamination factors of AgX was over 50 if an appropriate gas contact time was ensured even in the environment of steam condensation and the existence of hydrogen [8].

Recently, a novel idea has been proposed. AgX is expected to be used as an air-conditioner filter. It is well known that HEPA filter and metal filter are customarily employed in central control room at NPPs. If AgX filter is used together with them, the safety will be greatly improved when an emergency occurs. This will benefit the operators as well as the residents around the nuclear facility. Furthermore, AgX filter can be applied to a mobile filtering system. Since this system can be wholly mounted on a track, it can be easily used at the places where the track can go. This is very useful when a severe accident happens.

In addition to above applications, AgX filter can be used to SGTS, annulus, reprocessing plants, place of fuel handling and storage of nuclear fuel. Furthermore, AgX and AgR are also serviceable in anti-earthquake and preventing terrorist activities because their filter units can be designed in a small size and installed under the ground.

4. Conclusions

AgX and AgR as organic iodine adsorbents have been developed and their adsorption characteristics have been evaluated. The results show that these adsorbents not only have the high adsorption efficiencies of organic iodine, but they also can be operated in hydrogen atmosphere. Especially, AgX can work in a broad temperature range from -5 °C to 150 °C, and AgR in high hydrogen content of 10 vol%. The long-term storage experiment shows that AgX and AgR are stable at outdoor temperature and 100% relative humidity. The results of heat- and steam-treatments at high temperature show their good thermal stability. In view of the excellent performances of AgX and AgR, they will serve more nuclear facilities.

5. References

[1] D. J. Morgan and A. Morgan, Studies on the Retention and Metabolism of Inhaled Methyl Iodine-I, Health Physics 13 (1967)1055-1065.

[2] A. Morgan, D. J. Morgan, J.G. Evans and B.A. Lister, Studies on the Retention and Metabolism of Inhaled Methyl Iodine-II, Health Physics 13 (1967) 1067-1074.

[3] D. A. COLLINS, L. R. TAYLOR and R. TAYLOR; the developments of impregnated charcoals for trapping methyl iodide at high humidity, TRG Report, 1300 (W) (1967).

[4] J. F. Wang, T. Kobayashi and K. Endo, Properties and Applications of Silver Zeolite (AgX), Proceedings of 2nd International Conference on Maintenance Science and Technology (2014), pp.133-134.

[5] Jifeng Wang, Toshiki Kobayashi, Yuichiro Uzuyama and Koji Endo, Adsorption Characteristics of Radioactive Organic Iodine on AgX. The 11th International Topical Meeting on Nuclear Reactor Thermal Hydraulics, Operation and Safety. Gyeongju, Korea, October 9-13, 2016. Paper No: N11P0411.

[6] J. F. Wang, Y. Ishikawa, Y. Uzuyama, T. Kobayashi and K. Endo, Development of High-Efficiency Adsorbents for Organic Iodine Removal. Proceedings of 3rd International Conference on Maintenance Science and Technology for Nuclear Power Plants (2016), pp.58-59.

[7] U. S. Nuclear Regulatory Commission, methods and assumptions for evaluating radiological consequences of design basis accidents at light-water nuclear power reactors. Regulatory guide 1.195 (2003).

[8] S. Kawamura, T. Kimura, F. Watanabe, K. Hirao and T. Narabayashi, Development of an Organic Iodine Filter for Filtered Containment Venting System of Nuclear Power Plants. Trans. Atomic Energy Society of Japan, J15.025, Advance publication by J-Stage (2016), *in Japanese*.