Application of Silver Impregnated Iodine Adsorbent to Nuclear Facilities*

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

**Hitachi Works, Hitachi-GE Nuclear Energy, Ltd.
3-1-1 Saiwai, Hitachi, Ibaraki, 317-0073 Japan
E-mail: tetsuo.fukasawa.gx@hitachi.com

*** Power & Industrial Systems R&D Laboratory, Hitachi, Ltd.
7-2-1 Omika, Hitachi, Ibaraki, 319-1221 Japan

Abstract
Radioactive iodine is one of the most important nuclides to be prevented for release from nuclear facilities and many facilities have off-gas treatment systems to minimize the volatile nuclides dispersion to the environment. Silver impregnated inorganic adsorbents were known as inflammable and stable fixing materials for iodine and the authors started to develop 25 years ago a kind of inorganic adsorbent that has better capability compared with conventional ones. Aluminum oxide (Alumina) was selected as a carrier material and silver nitrate as an impregnated one. Pore diameters were optimized to avoid the influence of impurities such as humidity in the off-gas stream at lower temperatures. Experiments and improvements were alternately conducted for the new adsorbent. The tests were carried out in various conditions to confirm the performance of the developed adsorbent, which clarified its good ability to remove iodine. Silver nitrate impregnated alumina adsorbent (AgA) has about twice the capacity for iodine adsorption and higher iodine removal efficiency at relatively high humidity than conventional ones. The AgA chemically and stably fixes radioactive iodine and fits the storage and disposal of used adsorbent. AgA is now and will be applied to nuclear power plants, reprocessing plants, and research facilities.

Key words: Silver Impregnated Iodine Adsorbent, Off-Gas Stream of Nuclear Facilities, Radioactive Iodine Removal, Alumina, Silver Nitrate

1. Introduction
Main radioactive iodine nuclides in nuclear facilities are I-131 and I-129 of which half-lives are 8.02d and 1.57×10^7y, respectively. As iodine is volatile and easy to disperse to the atmosphere, nuclear facilities remove radioactive iodine from their off-gas streams (1)(2). For nuclear power plants, iodine removal systems are used at reactor building as the standby gas treatment system and waste management building as the tank vent system. For reprocessing plants, iodine removal systems are used at each building which treats radioactive materials. Inorganic and organic iodine forms are detected in the off-gas streams of nuclear facilities. Chemical forms of I_2 and CH_3I are usually selected as representatives of inorganic and organic iodines, respectively.

There are wet and dry methods to remove radioactive iodine. The wet method is the alkaline solution scrubbing to absorb iodine in the solution and is used in many nuclear...
facilities such as French and Tokai reprocessing plants. The dry method uses iodine adsorption onto solid material and is used in Japanese nuclear power plants and Rokkasho reprocessing plants. Dry method comparatively shows higher iodine removal efficiency, less waste generation and stable iodine fixation.

Several solid adsorbents were known worldwide based on inorganic and organic carriers (3)-(5). As silver is easy to react with iodine, silver (impregnated) adsorbents were especially and widely developed such as silver zeolite, silver mordenite and silver silica gel (AgS). Most adsorbents physically react with iodine and only AgS chemically reacts with iodine. Chemical adsorption shows better iodine fixation with less reverse reaction. This property is important for long-lived iodine (I-129) adsorption. Iodine removal properties of AgS are excellent at high temperatures and decrease at lower temperatures. So the authors started the development of new inorganic adsorbent which can suppress this tendency.

2. Development of New Adsorbent

The investigation on the iodine removal efficiency decrease at lower temperatures revealed that the inlets of small pores of AgS were covered by impurities like moisture (small pores have large surface area and effectively act as iodine adsorption site). Silica gel is also known as moisture adsorption material, so other materials were considered as a carrier and alumina was chosen for suitable carrier material.

The influence of pore diameters of silver alumina (AgA) on iodine (CH$_3$I: 1-1000 ppb) removal efficiency in Fig. 1 shows the highest decontamination factor (DF) at about 60nm in case of 90% relative humidity (RH). Decontamination factor of DF$_{5cm}$ is defined as the ratio of inlet to outlet iodine concentrations in the off-gas streams with the adsorbent column thickness and diameter of 5cm (about 100g of spherical AgA). The DF decrease for smaller pores is considered to be due to moisture blockage and for larger pores to surface area decrease. Smaller pores are important to increase DF at higher temperatures (lower RH), so both ~10nm and ~60nm pores are prepared on the alumina carrier (6).

Various silver compounds were tested after their impregnation onto alumina carrier. As shown in Fig. 2 (same column conditions as Fig. 1), the experiments revealed that solubility of the compound affected the iodine (CH$_3$I) removal efficiency at lower temperature (~30C) and silver nitrate showed the highest efficiency in the case of 90% RH. This tendency seems to be caused by the more effective reaction of CH$_3$I with silver solution than moisture-covered solid silver at high humidity.
Silver nitrate impregnation amounts are optimized experimentally to be 8-24 wt% of silver (metal). In order to minimize the waste volume higher silver concentration is preferable because of more iodine adsorption in the same amount of AgA (silver content has little affect to AgA cost). Higher silver content AgA showed silver nitrate crystallization on the adsorbent surface (out of pores) after alternate high and low humidity conditions. The dissolved silver nitrate solution seemed to come out from the pores at high humidity and to be converted to crystal at low humidity. Thus low humidity conditions are necessary for higher silver content AgA during its utilization. Lower silver content AgA never showed such phenomenon. The optimum silver content was ~10 wt% (6).

3. Application to Power Plants

The performances of developed AgA were confirmed in order to apply AgA to the tank vent and standby gas treatment systems of boiling water reactor plants. The tank vent conditions are low temperature (~30°C), high humidity (0-90% RH) and many impurities (SOx, NOx, etc.) in the off-gas stream. Simulated off-gas experiments were conducted with various impurities of predicted actual concentrations, which clarified that the AgA could obtain higher DF than required value of 10 in all cases. The test results were finally confirmed by using actual off-gas and mock-up apparatus with longer test periods. Actual off-gas test showed that the DF for AgA was about 40 even after 1200 days exposure. Figure 3 (same column size as Fig. 1) shows the test results of AgA and other adsorbent (AgX: silver zeolite) at 70% RH. Thus several plants already installed AgA in tank vent system without any iodine release to the environment (7).
Fundamental tests were also performed to apply AgA to the standby gas treatment system (SGTS) of the nuclear power plants. SGTS is used to prevent radioactive iodine release assuming various accidents including LOCA (loss of coolant accident) and expected to get DF of more than 34 at wide iodine concentrations (0.001-100 ppb) during the accident period (max. 80 days). Simulated test results showed that DF of AgA had no iodine (CH3I) concentration dependency and were more than 1000 even after 100 days air exposure. These results demonstrate the applicability of AgA to SGTS.

4. Application to Reprocessing

Radioactive iodine is mostly released from the spent nuclear fuel at the shearing and dissolution processes of reprocessing. The off-gas from these processes is collected and treated by the dissolver off-gas (DOG) treatment system. As reprocessing is carried out after several years cooling of spent fuel (4 years cooling for Rokkasho Reprocessing Plant), the main iodine nuclides are radioactive I-129 and stable I-127. The iodine removal system is operated at about 150°C to get high DF. AgA is known to achieve higher DF at higher temperatures. Iodine concentration is predicted to be 30,000 ppb (30 ppm) and required DF value is 250 (target DF: 1000) for DOG. The reprocessing plant also has VOG (vessel off-gas) and MOG (melter off-gas) treatment systems to prevent the release of residual I-129 and spontaneous fission product I-131 to the environment. As VOG and MOG systems have lower iodine concentrations and required DF, this study was mainly aimed at the AgA application to DOG system.

After many laboratory experiments, AgA was finally tested in the actual reprocessing plant WAK (Karlsruhe Reprocessing Plant) in Germany under the collaboration work with WAK and KfK (Karlsruhe Nuclear Research Center). The test results are summarized in Fig. 4. Column diameter was 2.5 cm and temperature was 140°C in this case. Relatively larger deviation of DF data at 2.5 cm and 5.0 cm bed depths might be attributable to smaller amount of AgA for iodine adsorption. AgA could obtain sufficient DF (actual iodine adsorption bed depth is more than 50 cm) during 118 days operation, which confirmed the applicability of AgA to the actual reprocessing plant. AgA has already been installed in the Rokkasho Reprocessing Plant, which is now doing the final hot tests using the actual spent fuel.

---

**Fig. 4** WAK test results for AgA
AgA of 10wt% silver has about 2 times higher iodine adsorption capacity per unit volume than AgS of 12wt% silver due to larger density of alumina than silica gel. Also the waste volume after saturated iodine adsorption for AgA is about 1/2 of AgS. Developed and commercially utilized AgA is shown in Fig. 5 with AgS. The amounts shown have equivalent iodine adsorption capacity.

![Fig. 5 View of AgA and AgS](image)

The stability of adsorbed iodine was also confirmed by heating and water immersion tests for AgA after saturated adsorption of I$_2$. Heating tests of ~100mg AgA at N$_2$ atmosphere showed little iodine desorption under 500°C. Water immersion test results in Fig. 6 indicate almost no iodine release for AgA after heating to 450°C. As I$_2$ is known to adsorb as forms of insoluble AgI and soluble AgIO$_3$ and AgIO$_3$ changes to AgI by heating, AgA with heat treatment drastically reduces the iodine release to water (9). Thus AgA is found to be also suitable for storage and disposal after use.

![Fig. 6 Water immersion test results for spent AgA](image)

5. Conclusions

The iodine adsorbent, silver alumina (AgA), has been developed in order to prevent radioactive iodine release to the environment from various nuclear facilities. The investigations started from the reaction mechanism of iodine with pre-prepared adsorbents by changing iodine concentration, temperature, impurity concentration. Various laboratory tests and actual plant tests revealed the sufficient iodine removal efficiencies under the predicted and actual conditions, and the effectiveness of AgA application to the nuclear power plants and reprocessing plants. AgA is developed and currently utilized in nuclear facilities in Japan.
References