Countermeasure of Radioactive Organic Iodine in Filter Vent and Application of AgX in Japan

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Overview

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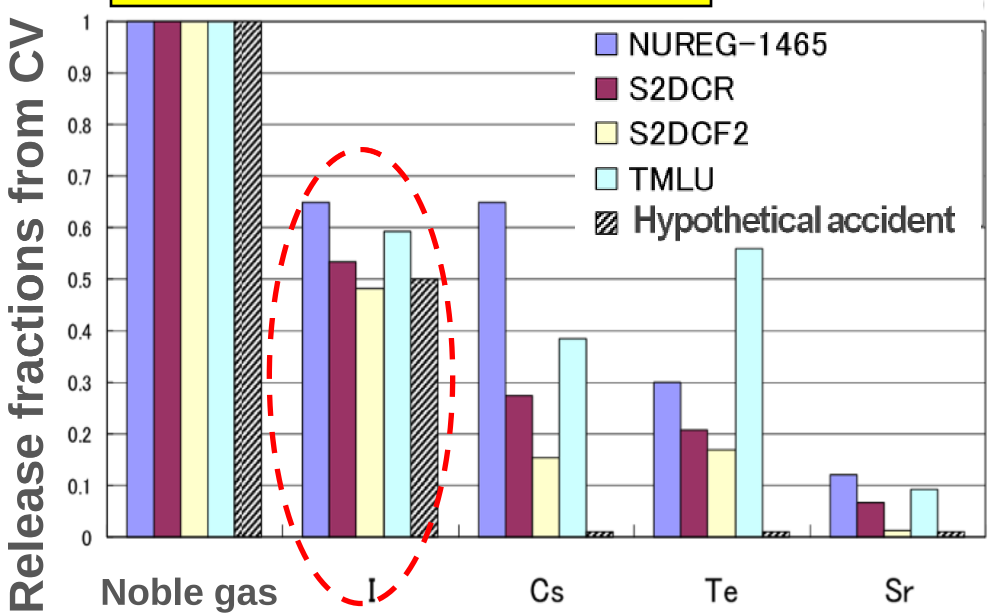
1. Background

Since the Fukushima Daiichi Nuclear Accident, the necessity to enhance the safety of nuclear facilities begins to be emphasized.

What kinds of radioactive waste will be generated and released when a reactor vessel is broken?

Doped-charcoal filter
High temp, RH, low capacity

Noble Gas
Hold-up System



Radioactive Aerosols
HEPA Filter
Metal Filter
Scrubber

Fig. 1 Comparison of source term after reactor vessel is broken for 1 hour. This picture is cited from a report of Japan Nuclear Energy Safety Organization issued in 2010.

Issues, Harmfulness and Countermeasures

Neglected issues

- Radioactive organic iodine is ignored due to traditional assumption that organic iodine content is only 0.15% of total radioactive emission.
- Phebus-FP Test and Japan Nuclear Energy Safety Organization reported the larger emission than expected value.
- A report from Three Miles shows that organic iodine content is more than 40% in radioactive emission.

Harmfulness of radioactive iodine

- As an air pollutant -very mobile throughout the environment.
- Severe toxicity compared to other radioactive wastes.
- Easy to be captured by human body and accumulated in thyroid gland.

Countermeasures of organic iodine in Japan

All nuclear power plants in Japan have taken countermeasures for radioactive organic iodine. Although Decontamination Factor (DF) is required over 50, many nuclear power plants aim the over 100.

Issues of Filter Vent

(1) Countermeasure of organic Iodine.
It is necessary to strengthen safety of around the nuclear facilities and to prevent the operator from being exposed to radiation.

(2) Countermeasure for hydrogen.
To reduce the risk of hydrogen combustion and explosion.
(H_2 concentration is high when vent starts to work in WET process)

(3) Countermeasures of earthquake and terrorist activities.
The compact design is useful for anti-earthquake and -terrorist.

(4) Adsorption capacity deterioration due to the moisture condensation.
To prevent the performance deterioration of absorbent due to moisture condensation.

(5) Performance evaluation of reactor in different atmospheres.
Boiling Water Reactor (BWR): nitrogen atmosphere.
Pressurized Water Reactor (PWR): air atmosphere.

To overcome above issues, adsorption characteristics of silver zeolite (AgX) as an adsorbent of radioactive organic iodine have been evaluated under the harsh conditions since the Fukushima Daiichi Nuclear Accident.

2. Objectives

(1) To discuss the properties of silver zeolite (AgX) as a radioactive iodine adsorbent.

(2) To introduce adsorption characteristics of radioactive iodine under high humidity, temperature and pressure.

(3) To describe the characteristic of removing hydrogen.

(4) To introduce the applications of AgX to filter vent at nuclear power plants in Japan.

3. Experimental methods and results

AgX Crystal Structure

AgX is a compound that Ag ions replace those metal ions in zeolite.

Zeolites are highly crystalline alumino-silicate frameworks. Si and Al atoms are joined by an oxygen bridges. Above 650°C, zeolites will lose long-range order and show amorphous properties.

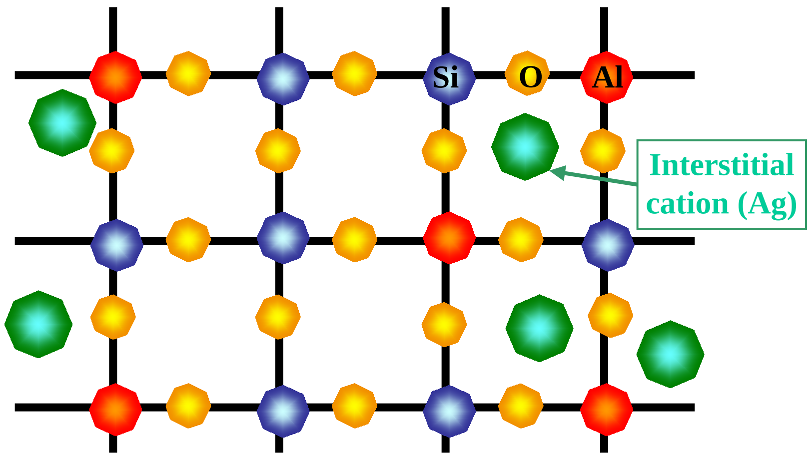


Fig. 2 Atom arrangement in zeolite.

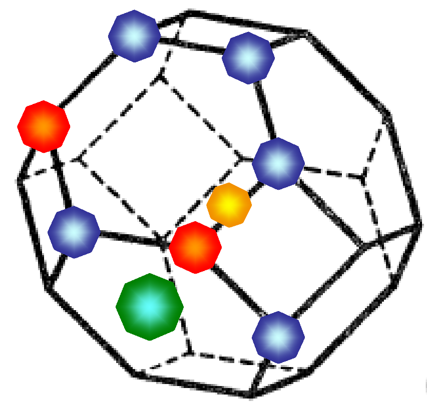
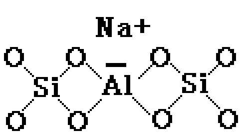


Fig. 3 β-cage containing a cation.

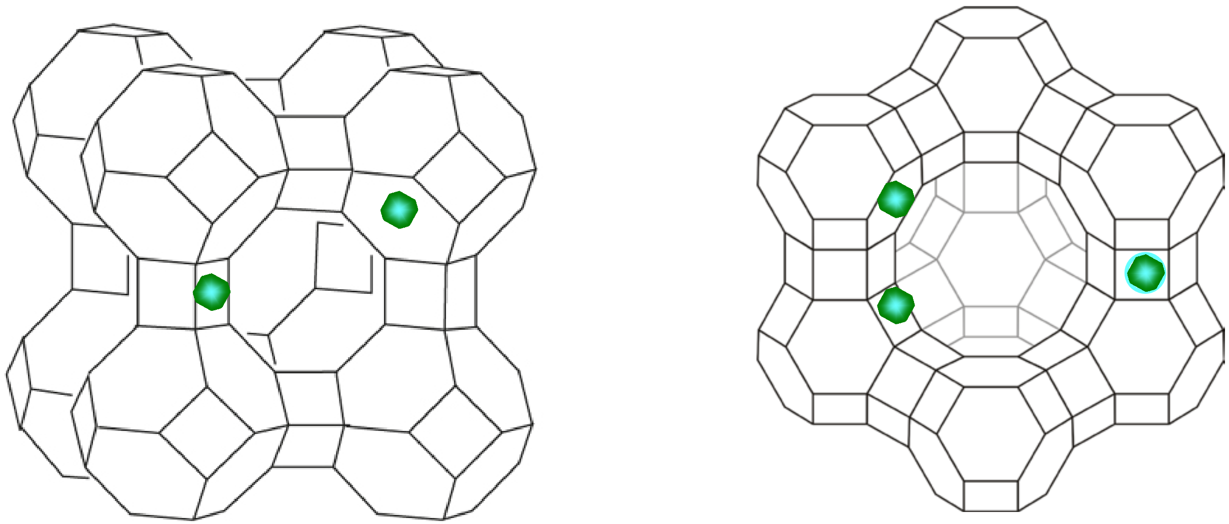
Al and Si atoms occupy vertex; O atoms lie in the center of the side.
$[AlO_2]^-$unit exhibits negative valence and it requires counter ions to neutralization, for example Ag cation (green dot in figure).

Number of Al atom= Number of cation

$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]\cdot nH_2O$



Position and Importance of Ag Ions



A-type X, Y-type

Fig. 4 Typical silver-zeolites.

Two electron pairs of oxygen act with Ag ion. As a result, Ag ions enter into 4-membered, 6-membered, 8-membered and 12-membered rings. Otherwise, Ag ions occupy the inside and outside of sodalite cage.

It is important to prepare an AgX product with good reproducibility in Ag ion concentration and suitable atom arrangement

Reaction Mechanism

Roll of Ag: Ag is known for its ability to grab and immobilise iodine. Actually, the reaction mechanism between AgX and methyl iodine is not clear until now. There are very few papers on it. The following description is only our speculation according to our experimental results.

It is reported that methanol and dimethyi are formed after the methyl iodine is adsorbed by AgX. If it is true, the following reactions can be written.
In the case of ethyl iodide, ethanol is formed.

$$CH_3I + H_2O + Ag^+ \rightarrow AgI + CH_3OH + H^+ \quad (1)$$

$$CH_3I + CH_3OH + Ag^+ \rightarrow AgI + CH_3OCH_3 + H^+ \quad (2)$$

Our experimental results show that methanol is formed by detecting condensation water of steam that adsorbed methyl iodine. But Methane, ethane, propane, dimethyl ether and diethyl ether are not detected.
The formation ratio of methanol is roughly estimated to be around 85% by calculating the amount of the adsorbed methyl iodide and formed methanol.

Effect of Moisture on Adsorption Characteristics

Adsorption characteristics of methyl iodide is affected by water vapor content in the atmosphere. Adsorption efficiency becomes poor in low Dew Point Distance (DPD) or high humidity.

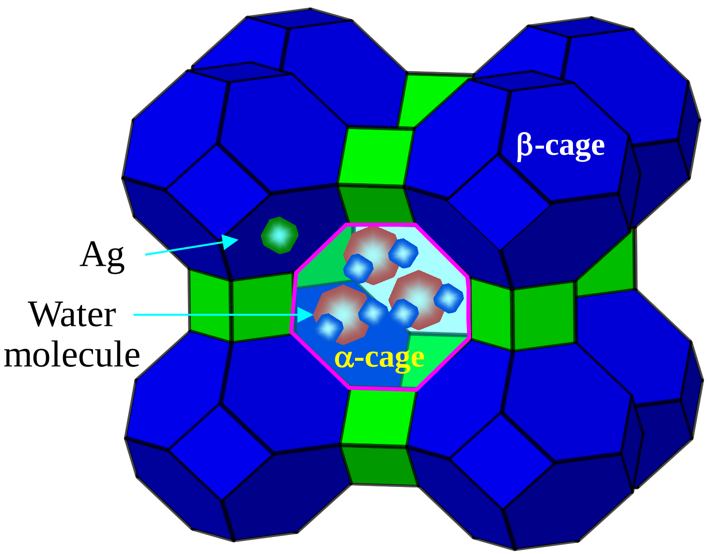


Fig.5 A-type silver-zeolite.

Almost the water molecules are adsorbed in α-cage.
If Ag ions exist, water molecules are likely to be gathered around them.

However, there is a spatial limitation in accommodating water molecules in the large cage. This large cage only accommodate 3 water molecules in A-type and 6 water molecules in X or Y-type.
(The molecules can not pass through the large cage)

As a result, the water molecules in large cage inhibit the access of methyl iodine to Ag ions. Therefore, adsorption efficiency becomes poor at high humidity.

If Ag content is not high enough, the adsorption efficiency becomes poor immediately in high humidity.
(Difference in adsorption performance is important under high humidity for different type zeolites.)

High Adsorption Efficiency at Low DPD*

Table 1 Adsorption efficiency of CH_3I at different DPD (Steam:Air=95:5, radioactive I-131).

Bed depth (mm)	Residence time (sec.)	Adsorption efficiency of CH_3I (%)		
		DPD 5K (104°C)	DPD 10K (109°C)	DPD 15K (114°C)
50.8	0.16	99.9140	99.9640	99.9900
76.2	0.24	99.9740	99.9901	99.9981
101.6	0.32	99.9890	99.9989	99.9991
127.0	0.40	99.9932	99.9994	99.9996

External testing results

High adsorption efficiencies can be still obtained although the DPD is as low as 5 K

DPD*: Dew Point Distance

Adsorption Efficiency of CH_3I under Harsh Conditions

Table 5 Relationship between adsorption efficiency of CH_3I and bed depth. Testing conditions: LV*=20 cm/sec.; CH_3I=1.75 mg/m^3 (I-131).

Bed depth (mm)	Residence time (sec.)	Adsorption efficiency of CH_3I (%)
T=130 °C; RH=95 %; P=399 kPa**		
50	0.246	99.967
75	0.369	> 99.999
100	0.492	> 99.999

External evaluation results

AgX exhibits the high adsorption efficiency under the high temperature, humidity and pressure

**LV: Linear velocity; **RH: relative humidity*

Adsorption Efficiency, Comparison with Charcoal

Table 6 Adsorption efficiency of CH_3I at different conditions.

Bed depth (mm)	Residence time (sec.)	Adsorption efficiency of CH_3I (%)			
		RH 95%			RH 70%
		30 ºC	60 ºC	90 ºC	66 ºC
50.8	0.250	99.738	99.685	99.970	> 99.999
76.2	0.375	99.850	99.950	99.983	> 99.999
101.6	0.500	99.960	99.987	99.995	> 99.999

Testing conditions: P=103 kPa; LV=20.3 cm/sec.; CH_3I =1.75 mg/m^3 (I-131).

AgX is different from charcoal. It has several merits.

- It can work very well under high relative humidity, temperature and pressure.
- Without power supply.
- High adsorption capacity of CH_3I (>80 times larger than that of charcoal).
- High adsorption efficiency of CH_3I.
- Removal effect of hydrogen.
- Short residence time. As long as residence time is over 0.16 second, AgX can remove organic iodine effectively. This result has been proved under harsh conditions in BWR.

Removal Effect of Hydrogen

Table 5 Hydrogen concentration after the mixed gas (air + H_2) flowed through AgX.

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

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

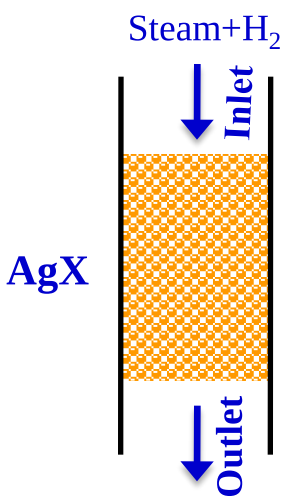


Fig. 6 Schematic of hydrogen content measurement.

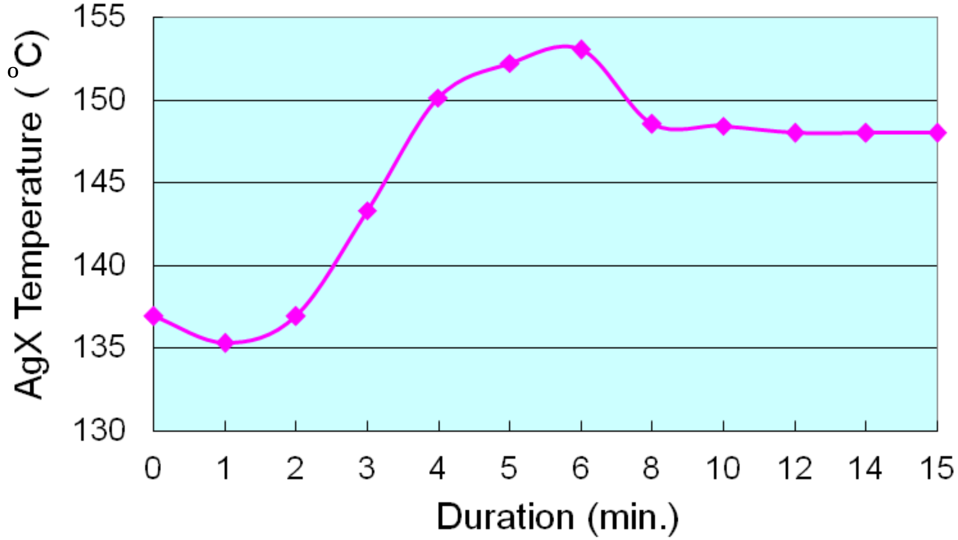


Fig. 7 Variations of AgX temperature with the duration that the mixed gas (air+H_2) continuously flows through AgX.

Vent Process from Start to Stability

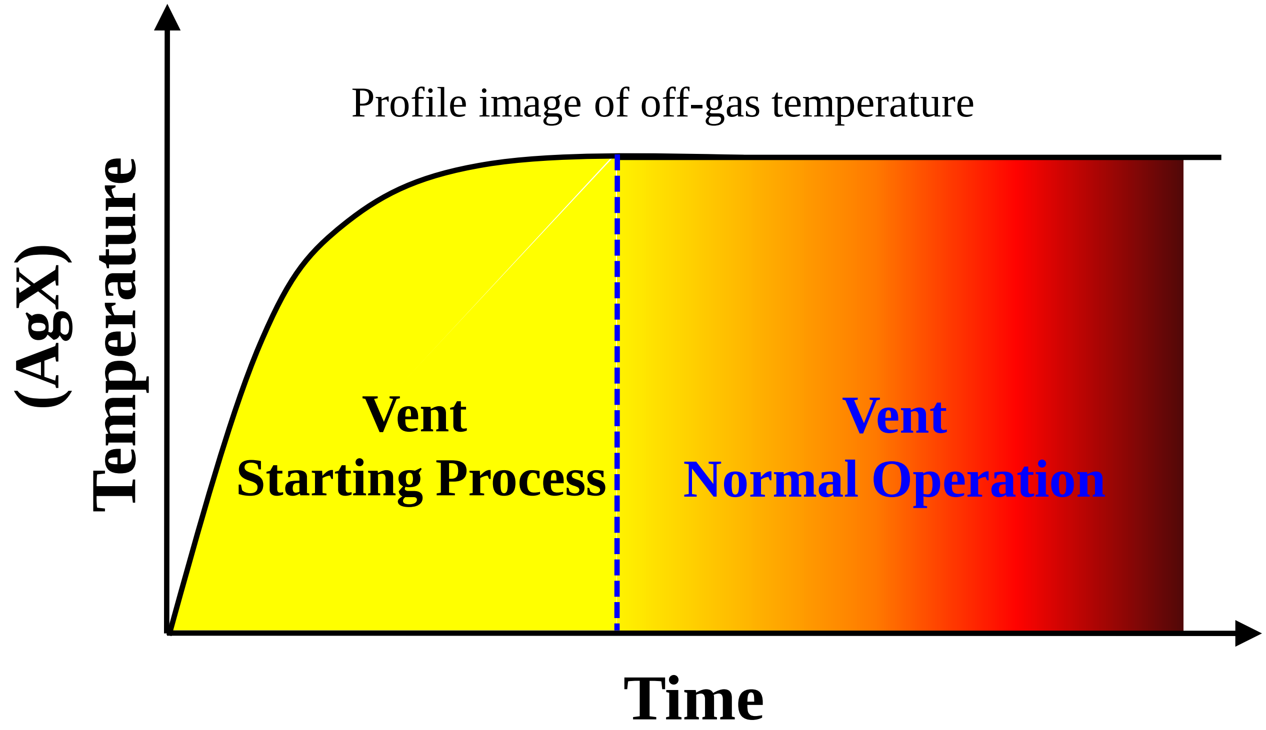


Fig. 8 Dependence of off-gas temperature on gas flowing time.

Evaluation Method of AgX

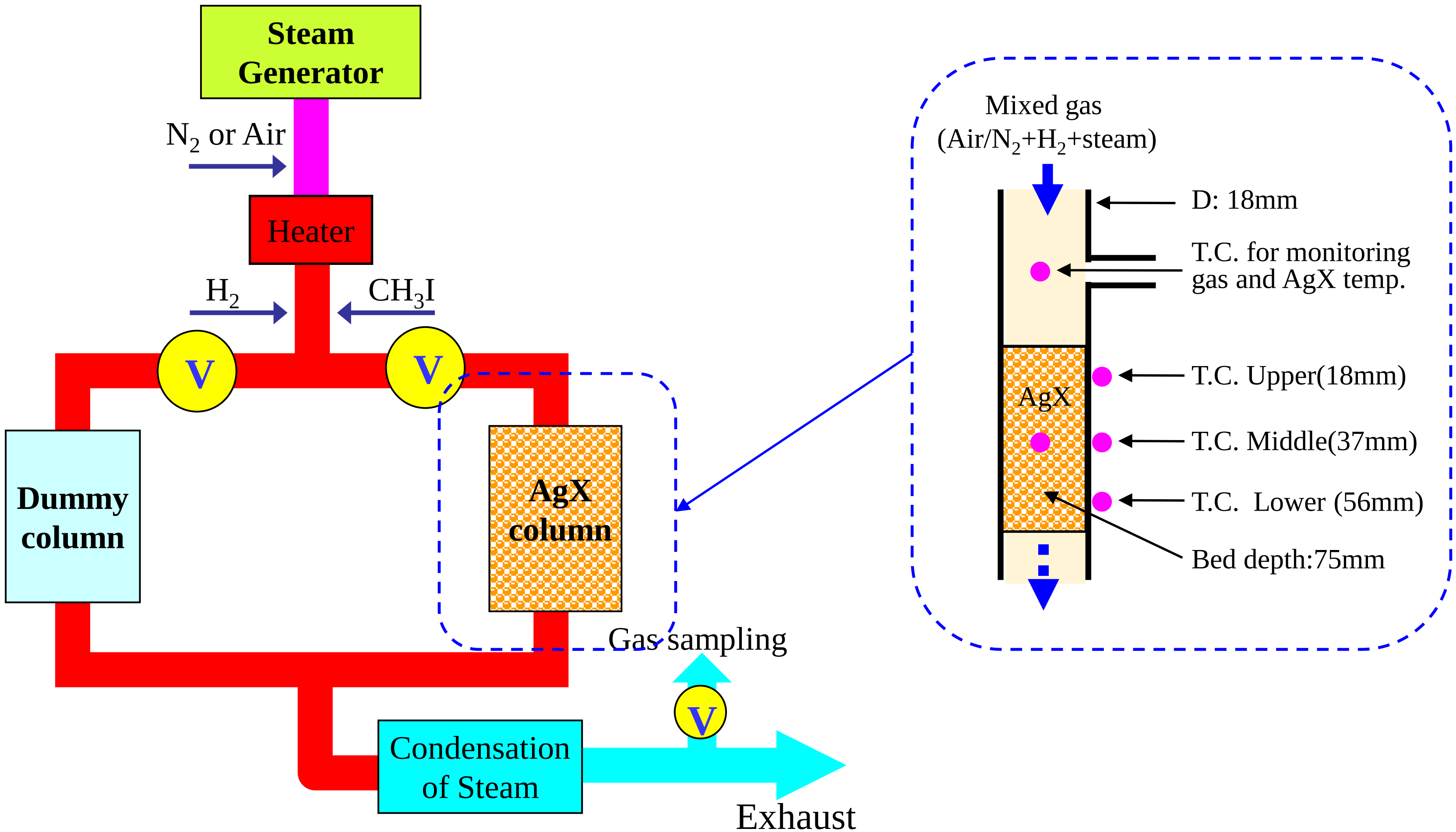


Fig. 9 An evaluation equipment for AgX adsorption efficiency. The superheated steam can flow through AgX rapidly.

Evaluation AgX When Vent starts (BWR)

Table 3 Gas composition. Vol.%

Time	H_2	N_2	H_2O
0-10	27	60	12
10-20	23	53	24
20-30	12	21	67
30-40	5	12	83

Table 4 Adsorption efficiency of CH_3I.

Time	Adsorption efficiency (%)
0-3	>99.6
3-6	>99.6
6-9	>99.6
15-18	>99.6
35-38	>99.8

Residence time: 0.18-0.21sec.

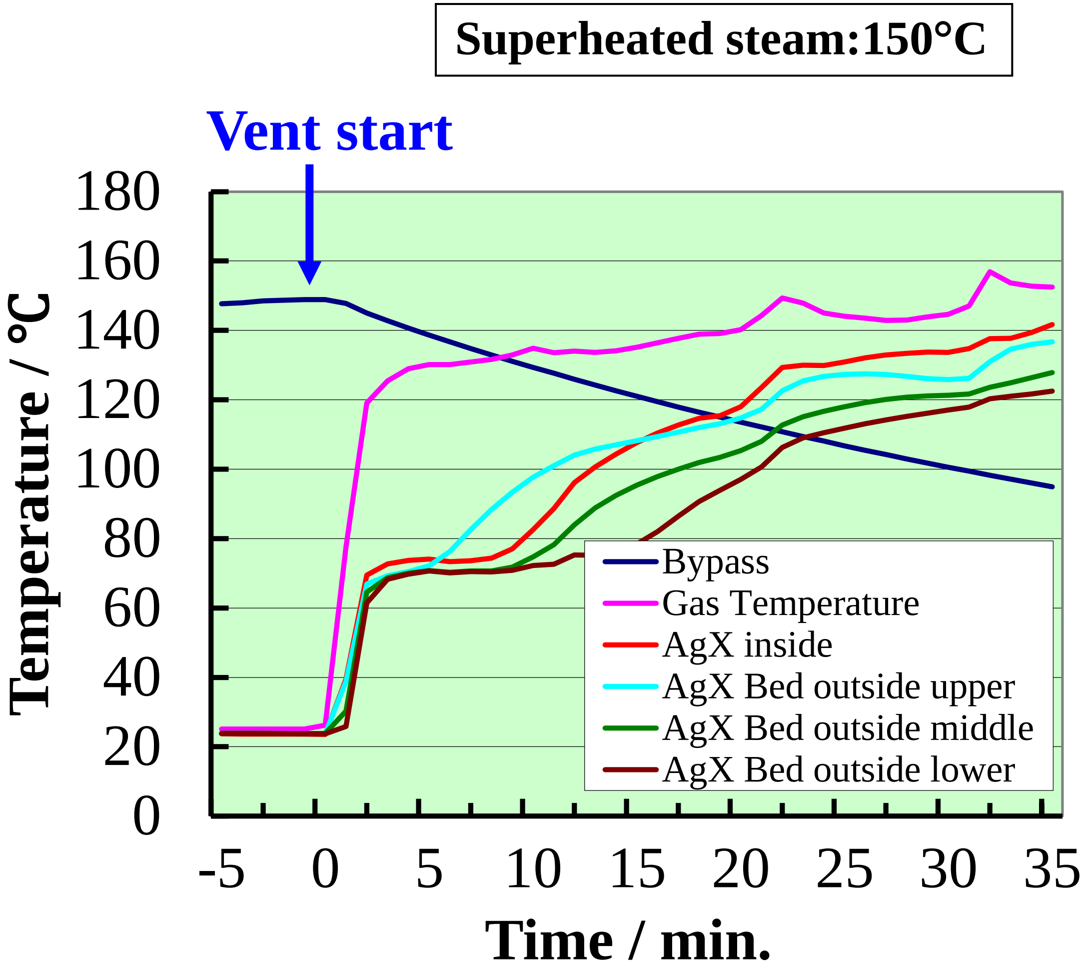


Fig. 10. Dependence of AgX temperature on gas flow time.

Evaluation AgX When Vent starts (PWR)

Table 3 Gas composition. Vol.%

Time	H_2	Air	H_2O
0-15	2.4	19	78
15-30	2.0	17	81
30-60	2.0	16	82

Table 4 Adsorption efficiency of CH_3I.

Time (min.)	Adsorption efficiency (%)
0-3	99.5
3-6	99.3
6-9	99.5
15-18	>99.8
35-38	>99.8

Residence time: 0.20-0.24sec.

Vent Start : Gas Temp. = 137℃

AgX : Water cont. = 6.3 %

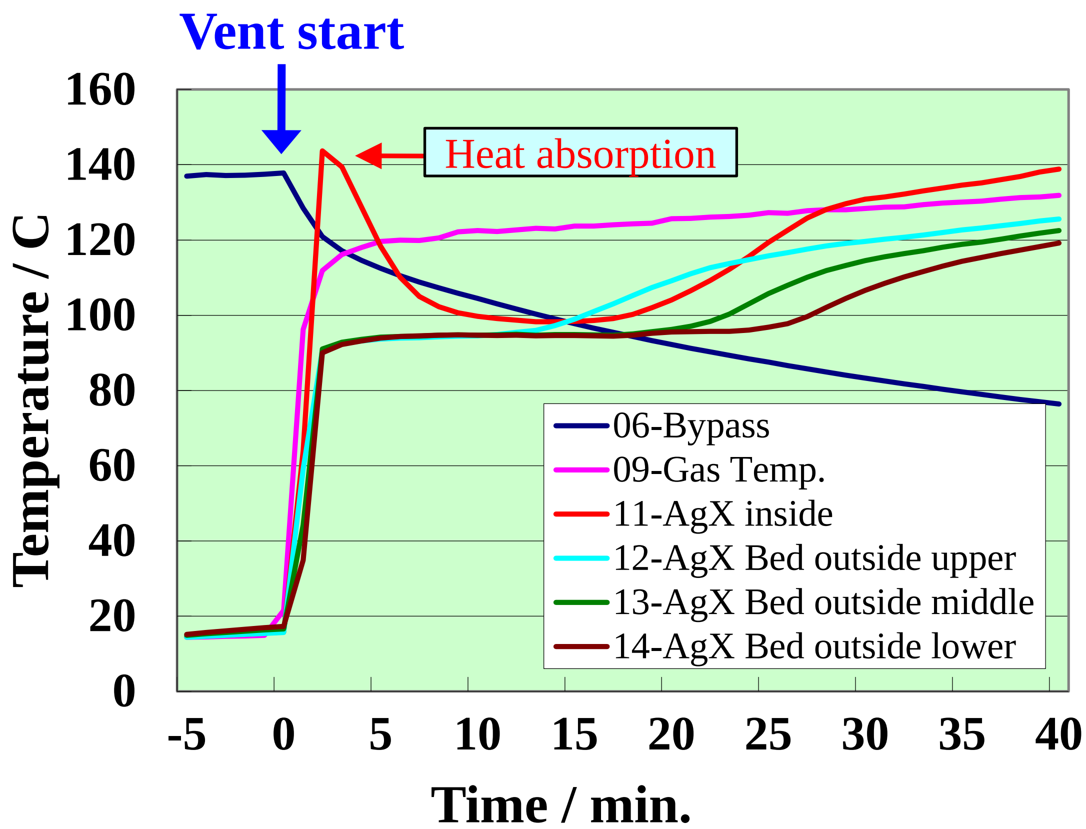


Fig. 11. Dependence of AgX temperature on gas flow time.

AgX Features

(1) High adsorption efficiency of radioiodine, especially organic iodine even under high temperature, humidity, and pressure.

(2) Adsorption capacity of CH_3I is in the range of 85-200 mg/g. The higher the temperature, the higher the absorption efficiency.

(3) High adsorption efficiency can be kept under following conditions.

- within 0.06 sec. residence time.
- after heat treatment (500 ºC) for ten days.
- after high temperature steam exposure (more than 100 ºC) for ten days.
- at the atmosphere containing hydrogen.

(4) Retention is over 99.9%. Adsorbed radioiodine can be retained almost completely.

(5) If AgX gets wet, its adsorption performance can be recovered by drying it.

(6) AgX has a function of removing hydrogen.

(7) Long product life cycle. Almost no aging deterioration under refrigeration or inert gas condition.

(8) Non-flammability. Secondary disasters such as fire will not occur.

Specifications of AgX

Table 6 Specifications of AgX produced by Rasa Industries, Ltd.

Items	Specifications	Remarks
Composition	Synthesized zeolite	
Metal cation of exchange	Silver (Ag)	
Silver content	> 36 wt%	Dry base
Particle size distribution	0.85-2.00 mm	JIS K 1474
Bulk density	1.2 g/ml (as is)	JIS K 1474
Loss on attrition	< 3 wt%	ASTM D-4058
Moisture content	< 12 wt%	150 ºC/3h dried

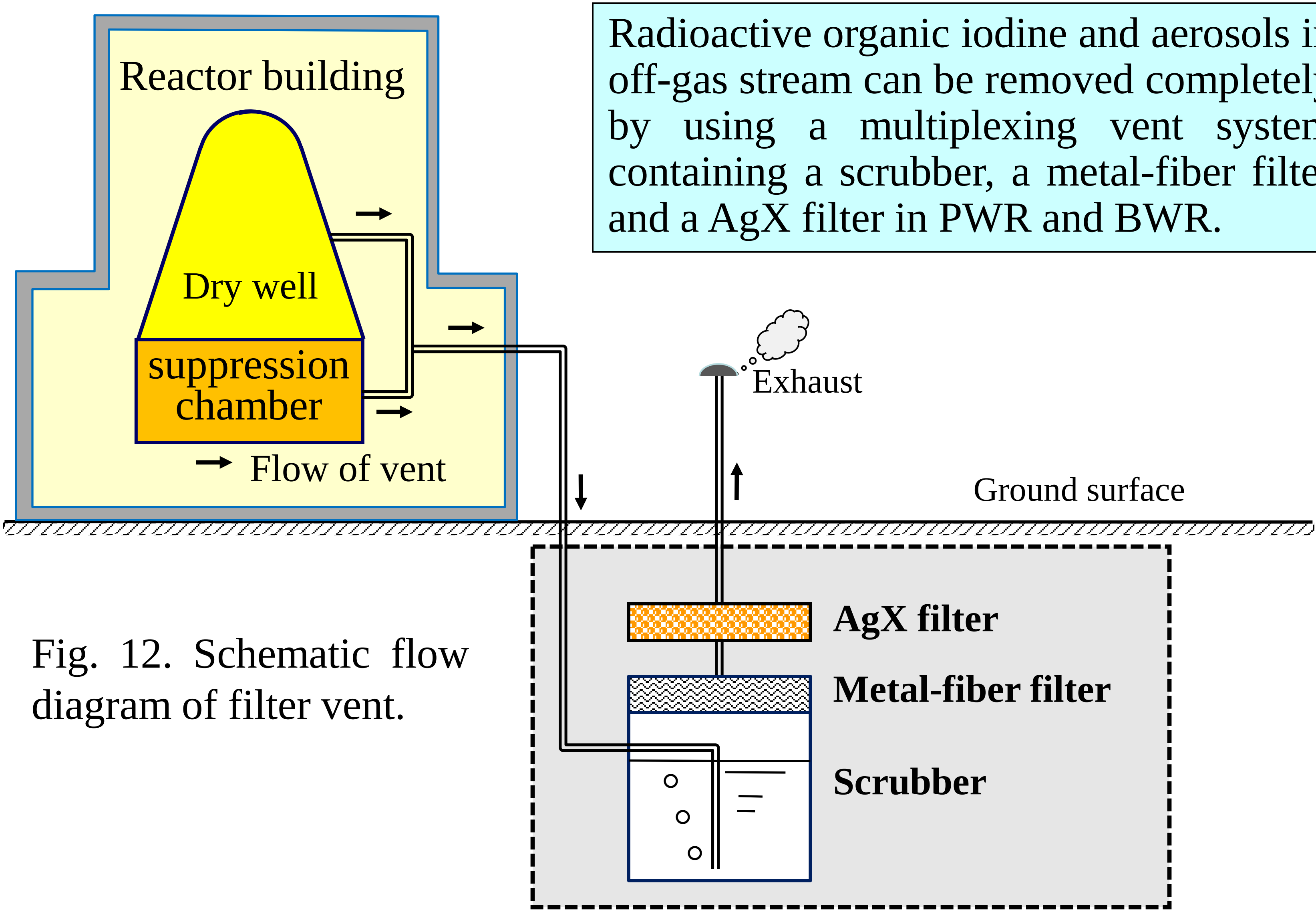
4. Application of AgX filter in Japan

Strengthening of Countermeasures

- Countermeasures of organic iodine are being strengthened in Stand-by Gas Treatment System (SGTS) and annulus.
- The multiplexing and diversification of SGTS are being considered in Japan.
- Effectiveness without power supply.
- Effective in the presence of water vapor.
- Effective even if hydrogen and oxygen exist (in the case of SGTS).
- Secondary disasters such as fire will not occur.
- Possibility of compact equipments (metal-fiber filter + AgX filter)
- Increasing processing capacity when an accident occurs
- Applying to central control room.
- And so on.

Countermeasure of Organic Iodine after WET Treatment

Radioactive organic iodine and aerosols in off-gas stream can be removed completely by using a multiplexing vent system containing a scrubber, a metal-fiber filter and a AgX filter in PWR and BWR.



Vent-filters can be designed underground

Fig. 12. Schematic flow diagram of filter vent.

AgX Filters are Used in Filtered-Vent System (DRY System)

The combined metal-fiber and AgX filter system can be used to remove aerosol and organic iodine.

AgX filter can be compacted and the adsorption performance can be enhanced.

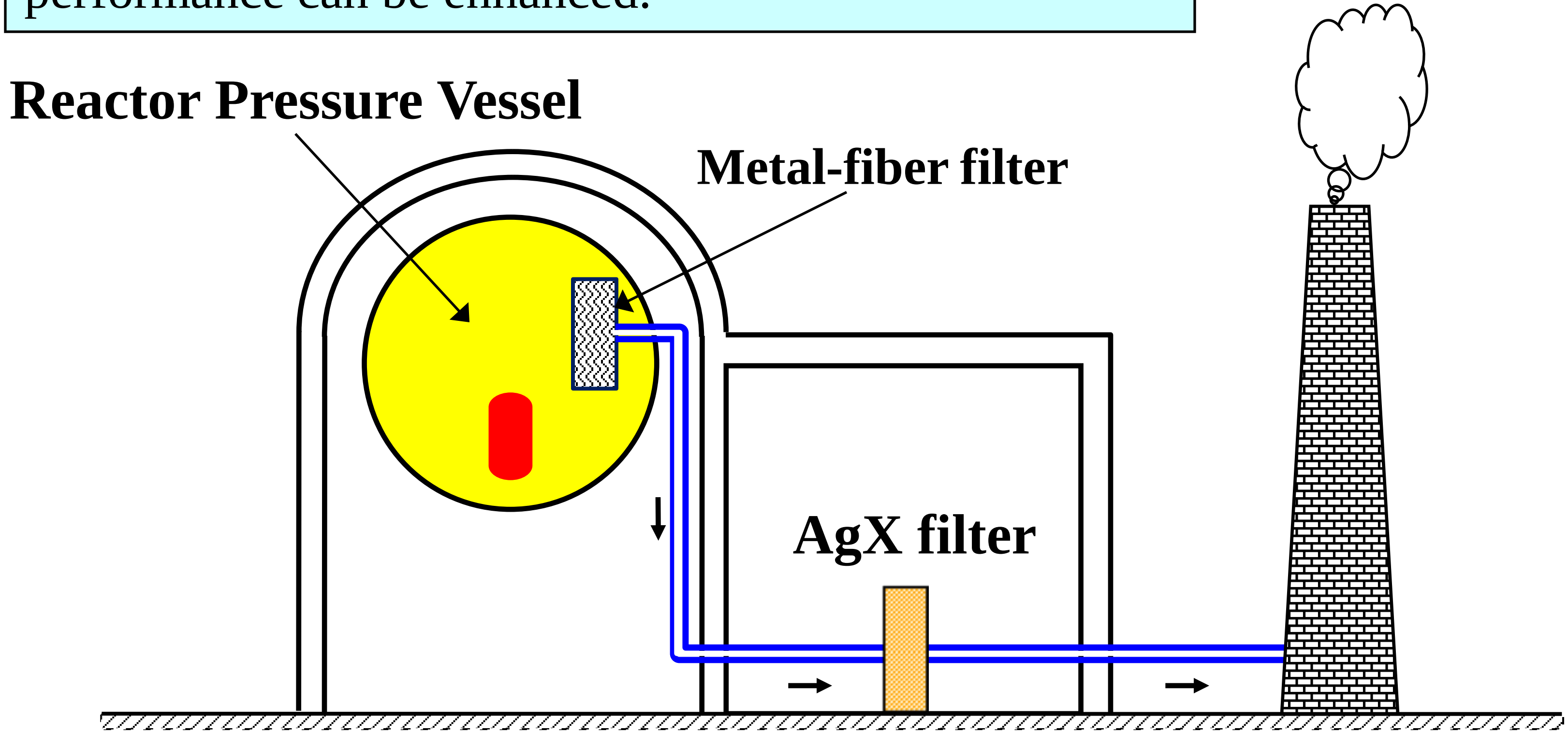


Fig. 13. Schematic view of filtered-vent system in PWR.

5. Conclusions and Our Proposals

Conclusions

- The evaluation results show that AgX has the very high adsorption efficiency of radioactive iodine under the harsh conditions such as high temperature, humidity and pressure.
- AgX also exhibits the effect of removing hydrogen.

Our Proposals

The most important thing is to minimize the impact on human even if the worst nuclear accident occurs.

Using AgX filter is an effective measure in preventing exposure of radioactive materials when a severe nuclear accident occurs.

Therefore, AgX can be used in nuclear facilities, such as SGTS, annulus and central control room.

AgX is expected to serve your nuclear power plant to capture radioactive iodine

Thank you for your attention