AgX for a Simplified FCVS and Other applications

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And

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Countermeasures at Japanese utilities after the Fukushima accident

- Prevention of the accident and measure to minimize damage in case accident occurs.
- Set primary importance on filtered vent. Multiplexing or installation in underground against Earthquake, Tsunami, Typhoon, and Terrorist attack.
- Measure for organic iodide. (DF ≧ 50)
- Multiplexing of SGTS and annulus.
- Set up central control room and emergency countermeasure room.

Overview

1. Metabolism of Iodine and Methyl iodine (from literature)
2. Background
3. Introduction of AgX
4. Experimental methods and evaluation results of AgX
5. TEPCO Filtered Venting System（AgX filter）
6. Application of AgX to Mobile cleaning system
7. Exploration of New Adsorbent-AgR
8. Conclusions and future work

Metabolism of Iodine

- In general, human body contains the iodine of 10~15 mg. 70-90% of iodine is retained in the thyroid.
- During the synthesis of thyroid hormones in the thyroid, iodide ions (I negative) are first converted into iodine molecules (I_2), then they are utilized.
- Iodine molecules or inorganic iodine compounds is retained in body easily and heavily by inhalation or ingestion. Retention rate is close to 100%.
- Absorption of iodine molecules or inorganic iodine compounds through the skin is small. (About 1%)
- The iodine retained in the body is almost excreted by urine.
- Biological Half-time of retained iodine in the body is about 31 days in the case of adult. (Individual difference is large)

Quoted from：CICAD No.72 Iodine and Inorganic Iodines ,Human Health Aspect (2009)

Some reports on the metabolism of molecular iodine and inorganic iodine compound can be looked up. Unfortunately, report of metabolism related to iodine of methyl iodide is very few.

The report about metabolism of methyl iodide will be introduced briefly.

Metabolism of methyl iodide (Experimental data of human body)

STUDIES ON THE RETENTION AND METABOLISM OF INHALED METHYL IODIDE—I

RETENTION OF INHALED METHYL IODIDE

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(*Received* 10 *October* 1966; *in revised form* 9 *March* 1967)

Abstract—Methyl iodide is one of the forms in which radioiodine may be released in accidents involving fission products. To provide information to assist in the assessment of the radiological hazard resulting from its inhalation, experiments were carried out in which volunteers inhaled iodine-132 labelled methyl iodide. Values of the retention ranging from 53 to 92% of the amount inhaled were obtained. The retention is highly dependent upon respiratory rate, low rates being associated with high retention and vice versa. To study the effect of respiratory rate and tidal volume on retention, additional experiments were carried out. These showed that there is negligible absorption in the respiratory dead space and that at normal breathing rates, absorption from alveolar air is incomplete. The average dose equivalent to the thyroid was about 3 mrem.

Experiment I was carried out in 18 volunteers (by UK)

In this experiment, iodine-132 was employed (half-life: 2.26 hours)

Relationship between respiratory rate and retention rate of methyl iodide was investigated.

The results showed that the low respiratory rate can result in high percentage retention.

Retention rate of methyl iodide from the breathing was averaged 72%.

STUDIES ON THE RETENTION AND METABOLISM OF INHALED METHYL IODIDE—II

METABOLISM OF METHYL IODIDE

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(*Received* 10 *October* 1966; *in revised form* 9 *March* 1967)

Abstract—Experiments are reported in which methyl iodide, labelled with iodine-132, was administered by inhalation to volunteer subjects to study the metabolism of the retained material. The fate of radioiodine administered in this way appeared to be very similar to that of radioiodine administered diagnostically as inorganic iodide. This was confirmed by a comparison of thyroid uptake and urinary excretion rates observed after administration of iodine-132 to the same subject by (a) inhalation of methyl iodide and (b) ingestion of sodium iodide. It appears therefore that *in vivo*, methyl iodide is broken down very rapidly, the organically bound iodine being converted to the iodide ion. The radiation dose to the thyroids of volunteer subjects from radioiodine uptake was quite small, averaging less than 20 mrem per experiment.

Experiment II was carried out in 4 volunteers. (by UK)

Iodine-132 was employed (half-life: 2.26 hours)

Metabolism of methyl iodide inhaled by the lung was investigated by comparing with NaI.

Metabolism of methyl iodide (Experimental data of human body)

Uptake into the thyroid

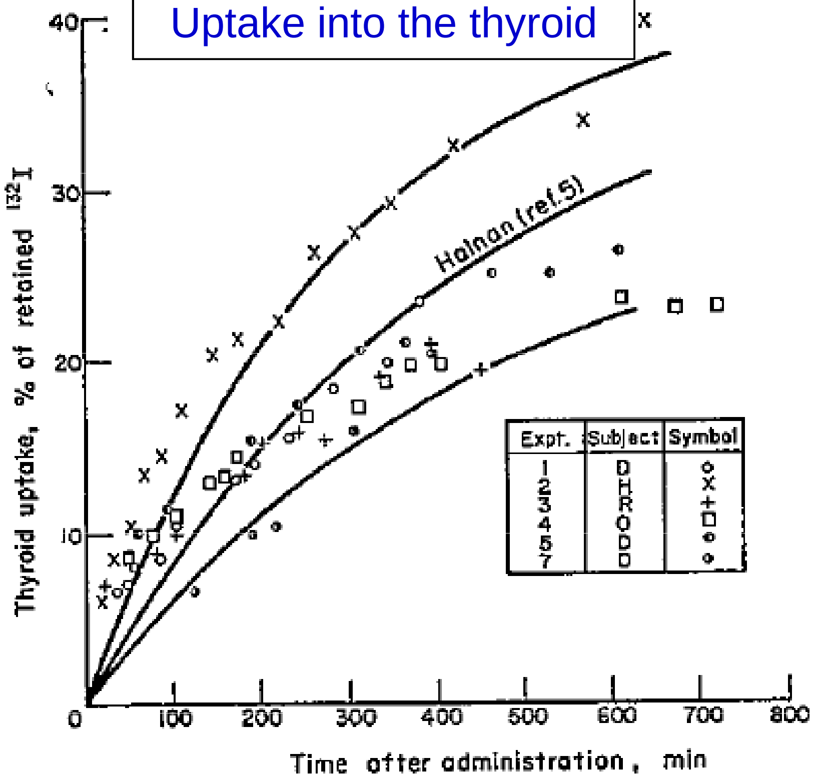


FIG. 1. Thyroid uptake of ^{132}I following inhalation of labelled methyl iodide.

Experiment II was carried out in 4 volunteers (by UK)

Iodine-132 was employed (half-life: 2.26 hours)

Vertical axis represents uptake of iodine-132 in thyroid (The ratio of the amount of uptake into the thyroid to inhalation by the lung)

Horizontal axis represents the time after inhalation by the lung

Iodine of methyl iodide inhaled by the lung will be incorporated into the body and accumulates in the thyroid.

Quoted from
Studies on the Retention and Metabolism of Inhaled Methyl Iodine - Ⅰ
D. J. Morgan and A. Morgan , Health Physics Vol.13 pp1055-1065 (1967)
Studies on the Retention and Metabolism of Inhaled Methyl Iodine - Ⅱ
D. J. Morgan and A. Morgan et al, Health Physics Vol.13 pp1067-1074 (1967)

Metabolism of methyl iodide (Experimental data of human body)

Uptake into the thyroid

Excretion from urine

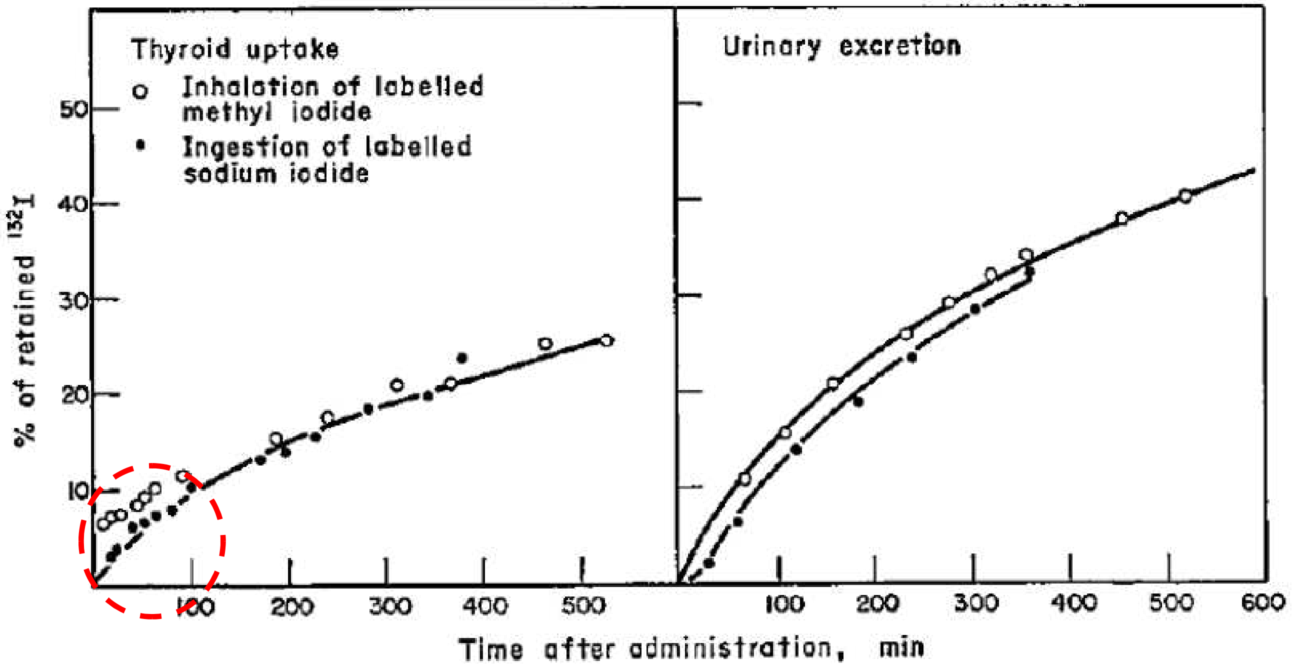


FIG. 5. Comparison of thyroid uptake and urinary excretion of ^{132}I after (A) inhalation as methyl iodide and (B) ingestion as sodium iodide.

○: Methyl iodide
●: NaI

Vertical axis represents uptake in thyroid and urinary excretion rate

Iodine-132 was employed (half-life: 2.26 hours)

Iodine in methyl iodide inhaled by the lung will be immediately incorporated into the body.
Then, the iodine will reach the thyroid by metabolic pathway like the way of NaI.
The part of the iodine is excreted by urine.

Metabolism of methyl iodide (Experimental data of human body)

Immediately after incorporation

Methyl iodide Inhalation from lung

NaI Ingestion from mouth

Vertical axis represents radiation counting rate at behind calf.

Iodine-132 was employed

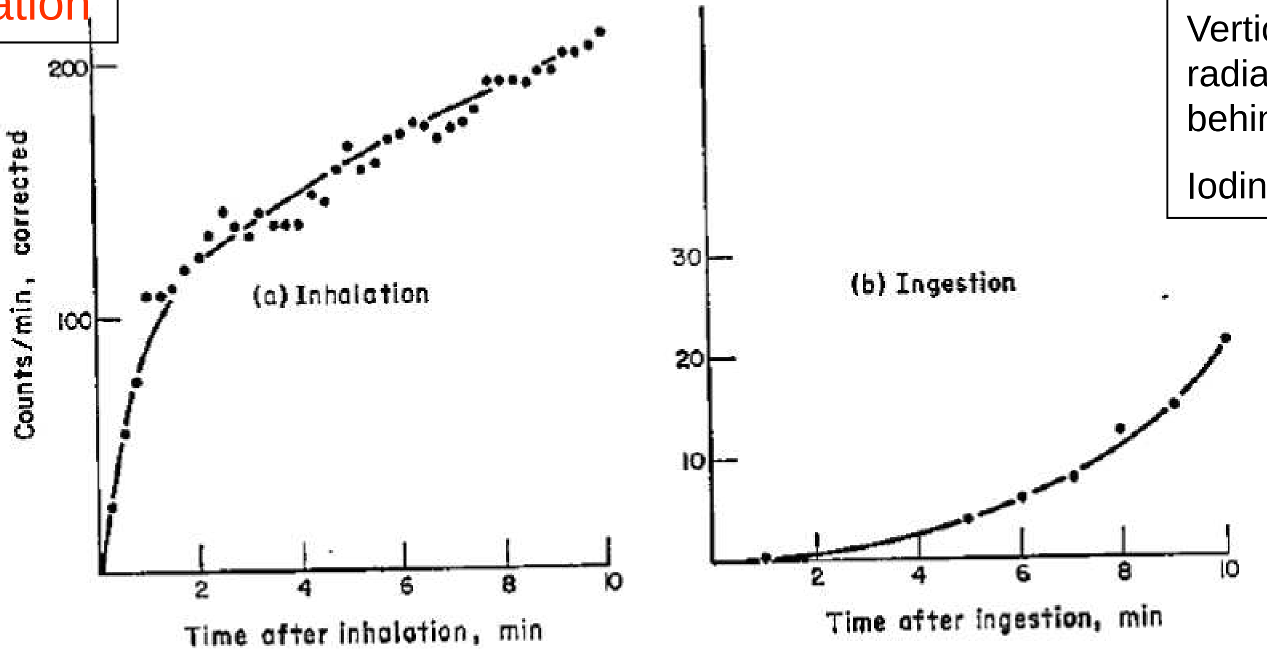


FIG. 6. Counting rate from shielded 9 in. dia. NaI crystal placed behind calf following (a) inhalation of methyl iodide and (b) ingestion of sodium iodide.

- Methyl iodide inhaled from lung will metabolize to thyroid in a few minutes. It is very faster than NaI ingestion from mouth.

Features of methyl iodide and importance of countermeasures

- Methyl iodide is a volatile gas with boiling point 42.5 °C. It cannot be removed by a common mask with removal function.
- Released methyl iodide is hardly adsorbed by plants and dispersed to the air. (ref. 1)
- In the Chernobyl accident, 70% of iodine species dispersed to Japan is organic iodine. (ref.2)

- Methyl iodide released from a reactor will widely disperse.
- It is very easy to incorporate with the body and will immediately migrate to the thyroid
- The human body will be contaminated by breathing in a few minutes.
- Owing to the less adsorption by natural substances, it is difficult to investigate pollution degree of methyl iodine later.

It is important to reduce the leakage of methyl iodine from the reactor.

References

1. D.H.F Arkina, R.C. Chadwick & A.C. Chamberlain , Health Physics Vol.13 p91 (1967)
2. H Noguchi and M Murata, J. Environ. Radioactiv., Vol. 7, p65–74D. (1988)

2. Background

Necessity of countermeasures in a severe accident

1. When a severe accident happens, off-gas in reactor containment vessel (RCV) must be opportunely released to atmosphere by venting systems in order to prevent RCV from breaking. To protect employees and local residents from radiological exposure, radioactive substances in off-gas must be removed by filters.
2. Radioactive substances in off-gas contain various radioactive aerosols, volatile gases.
3. Among these substances, organic iodine is especially emphasized because of its strongly toxicity and mobility.

Table 1 Solutions of Radioactive Substances in Venting Gas

Radioactive substances		Solutions
Noble Gas (Xe, etc.)		Hold-up System
Radioactive Aerosols (Cs, Te, Sr, etc.)		HEPA Filter Metal Filter Alkaline Scrubber
Radioactive Iodine	Elemental Iodine	Scrubber Doped-charcoal filter
	Organic Iodine	Doped-charcoal filter, ???

Features of Off-gas and Issues of Filter Vent

Features of Off-gas

- high temperature, high humidity, high pressure, large flow, coexistence of hydrogen (both of BWR and PWR).
- Especially, at the beginning of venting, **condensation of water vapor** will occurs due to the temperature difference between off-gas and adsorbent. Worryingly, condensed water vapor will affect adsorption performance of an adsorbent.

Issues of Filter Vent

- WET and DRY systems cannot remove organic iodine by a scrubber or metal filter (features of organic iodine: low boiling point, high volatility).
- Shortcomings of doped-charcoal filter: low capacity and efficiency, power supply, low relative humidity (RH).

An adsorbent with high adsorption capacity and efficiency under harsh conditions is required

3. Introduction of AgX

- **Adsorption characteristics of organic iodine on AgX**
  - high temperature, high pressure and high relative humidity
  - At the beginning of venting (water vapor condensation in filter vent system of BWR and PWR)
  - Conditions of SGTS and Annulus
- **Applications of AgX to nuclear facilities**
- **Future work**

4. Experimental methods and evaluation results

Evaluation- Adsorption Efficiency under the Harsh Conditions

Table 2 Relationships between absorption efficiency of CH_3I and bed depth at the high temperature, relative humidity (RH) and pressure. The evaluation was performed by NUCON International Inc.. Radioiodine: CH_3I (I-131) of 1.75 mg/m^3

Absolute pressure Relative humidity	**P=399 kPa, RH=95 %**		
Residence Time (Bed depth) / Temp.	0.125 sec. (50.8 mm)	0.187 sec. (76.2 mm)	0.250 sec. (101.6 mm)
110 (ºC)	99.748	99.978	>99.999
120 (ºC)	99.005	99.869	>99.999
130 (ºC)	99.673	99.843	99.974

AgX exhibits the high adsorption efficiency of CH_3 under the harsh conditions (high T, high P and high RH)

Adsorption Efficiency at Different DPD of AgX

Table 3 Adsorption efficiencies of CH_3I on AgX at various DPDs. CH_3I (I-131) serves radioactive iodine; gas composition is steam/air=95/5 (super heated gas); test pressure is fixed at 0.98 bar. These evaluations were performed by TÜV SÜD.

Bed depth (mm)	Residence time (sec.)	Absorption efficiency (%)				
		99 ºC (DPD* 0 K)	101 ºC (DPD 2 K)	104 ºC (DPD 5 K)	109 ºC (DPD 10 K)	114 ºC (DPD 15 K)
50.8	0.16	99.860	99.922	99.913	99.964	99.990
76.2	0.24	99.988	99.995	99.974	99.990	99.998
101.6	0.32	99.997	99.999	99.989	99.999	99.999

*DPD: Dew Point Distance.

High adsorption efficiencies can be obtained although the DPDs are as low as 0 K and 2 K

Adsorption Efficiency at Various Temperature and RH

Table 4 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). The evaluations were performed by NUCON International Inc.

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	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

The excellent adsorption performances demonstrate the applicability of AgX to SGTS and annulus.

Venting Process-from beginning to Stability

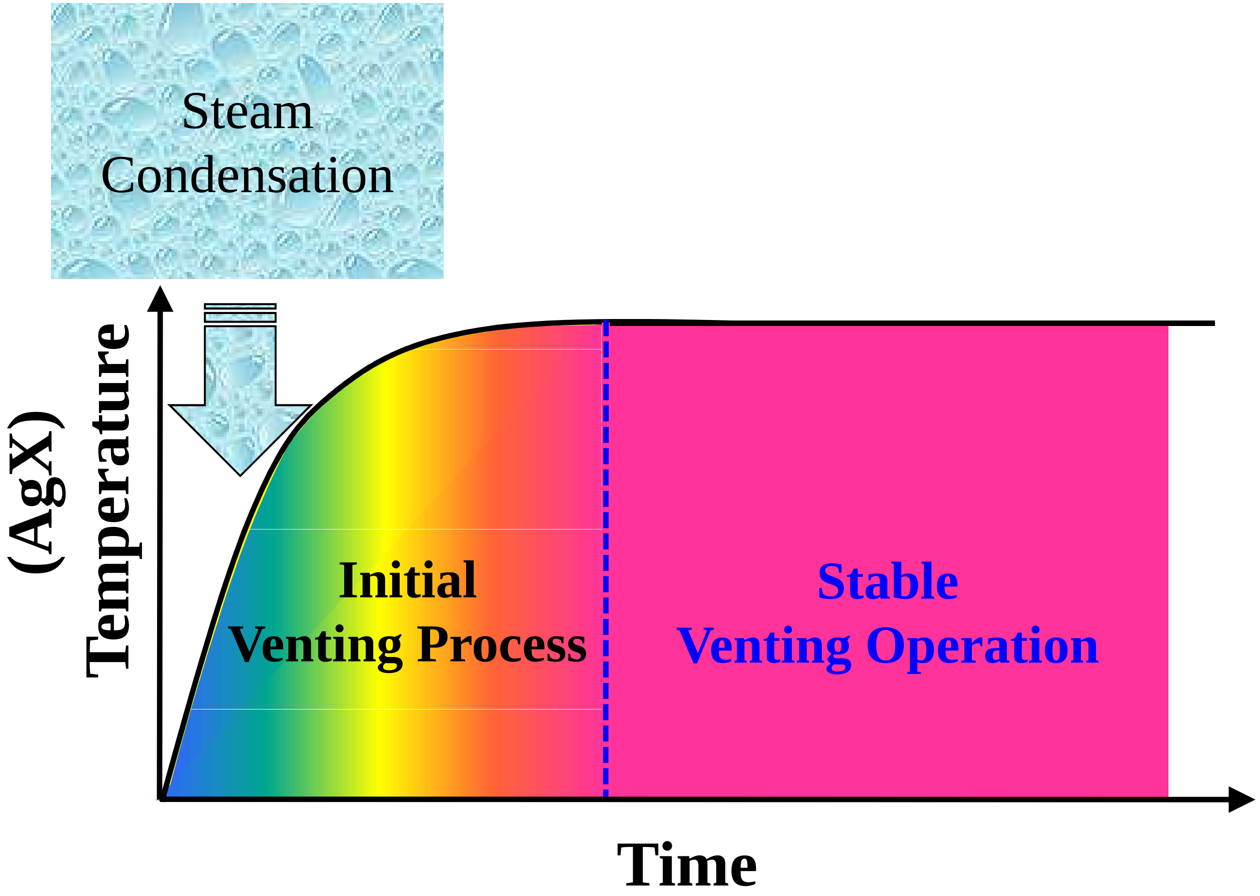


Fig. 3 Dependence of off-gas temperature on gas flowing time.

Evaluation Equipment of AgX

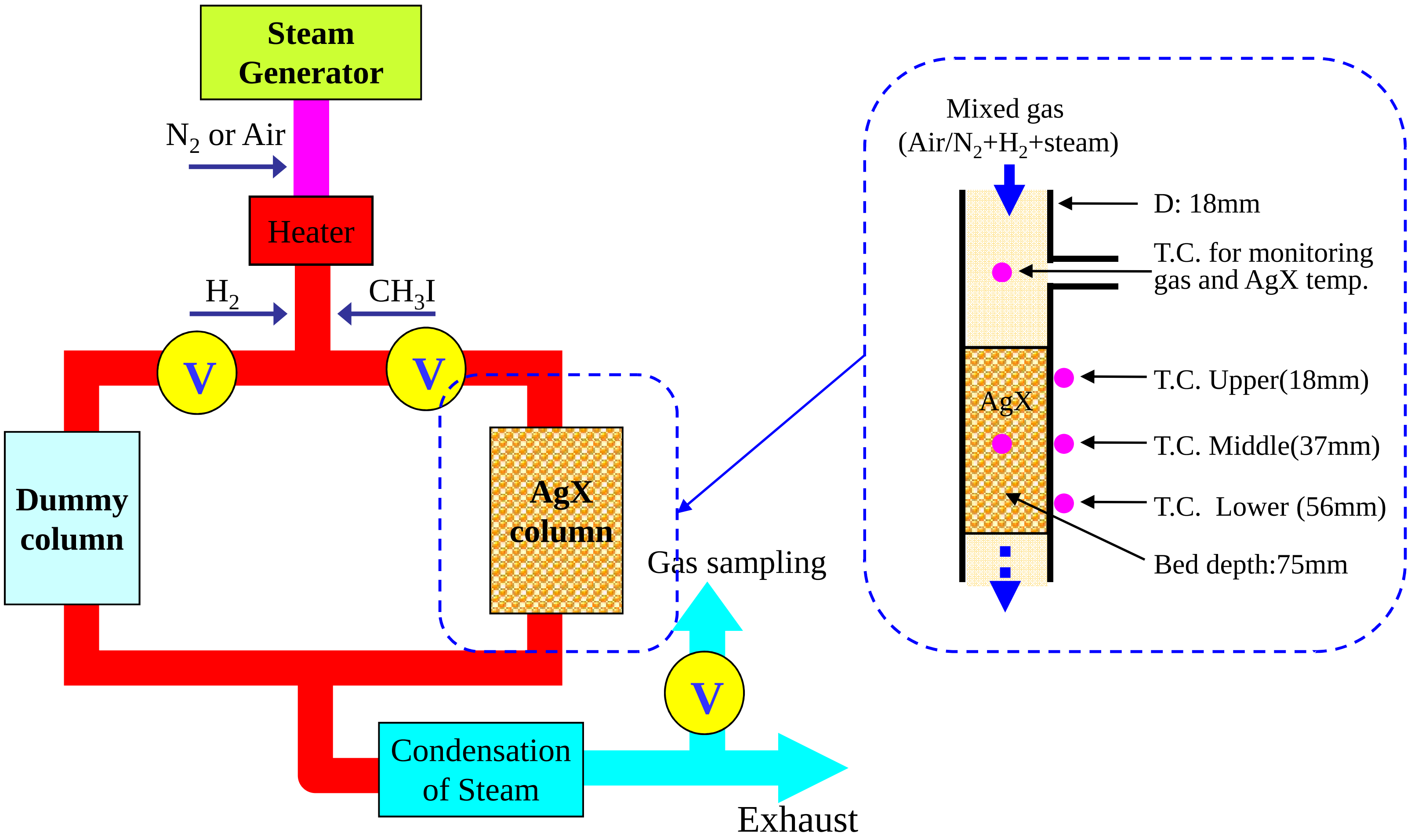


Fig. 4 Evaluation apparatus for AgX under varying gas compositions and temperatures. The superheated steam is used to create the varying environment.

Evaluation AgX When Venting Starts (BWR)

Table 5 Gas composition (Vol.%).

Time	H_2	N_2	H_2O
0-10	23	45	32
10-20	23	45	32
20-30	12	21	67
30-40	5	12	83

Dew point of initial gas: 71 °C.

Table 6 Adsorption efficiency of CH_3I.

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

Residence time: 0.18-0.21sec.

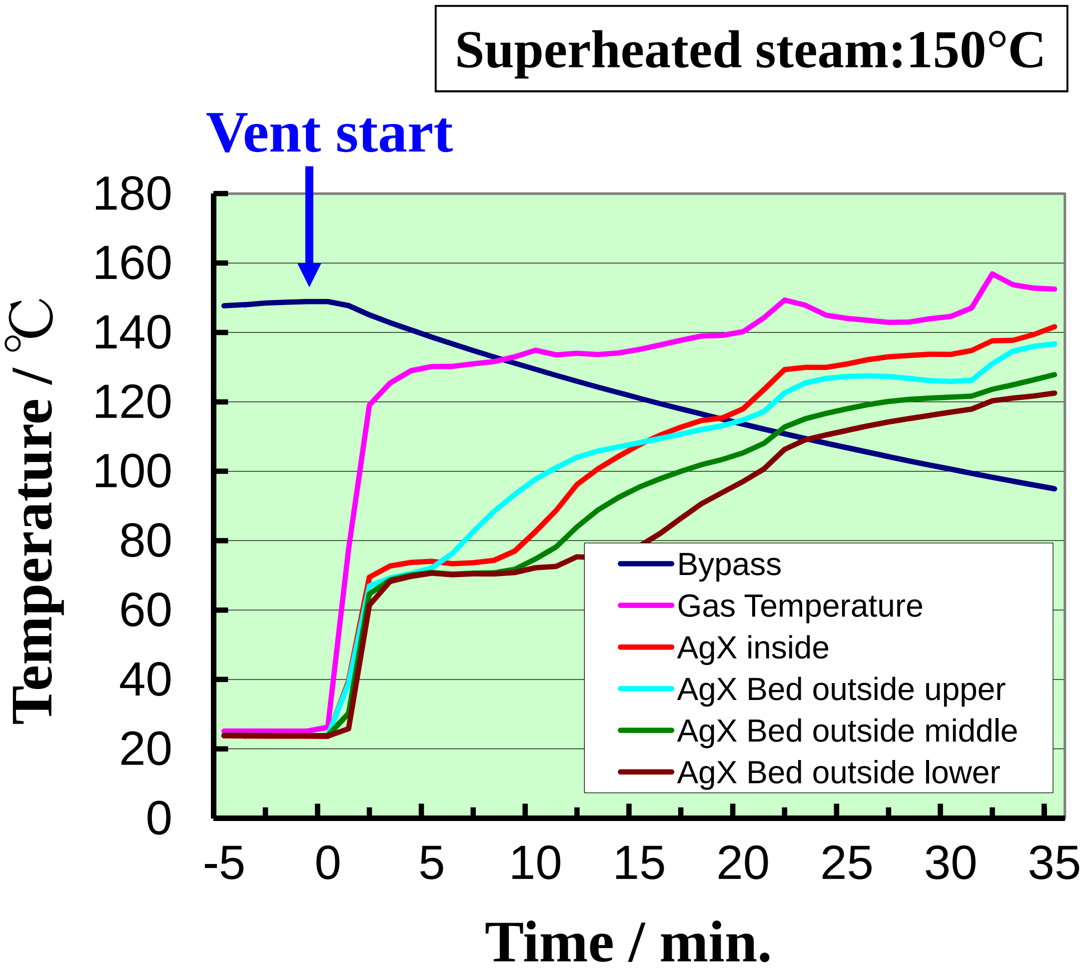


Fig. 5 Dependence of AgX temperature on gas flow time.

Evaluation AgX at the Beginning of Venting (PWR)

Vent Start: Gas Temp. = 137℃

AgX : Water cont. = 6.3 %

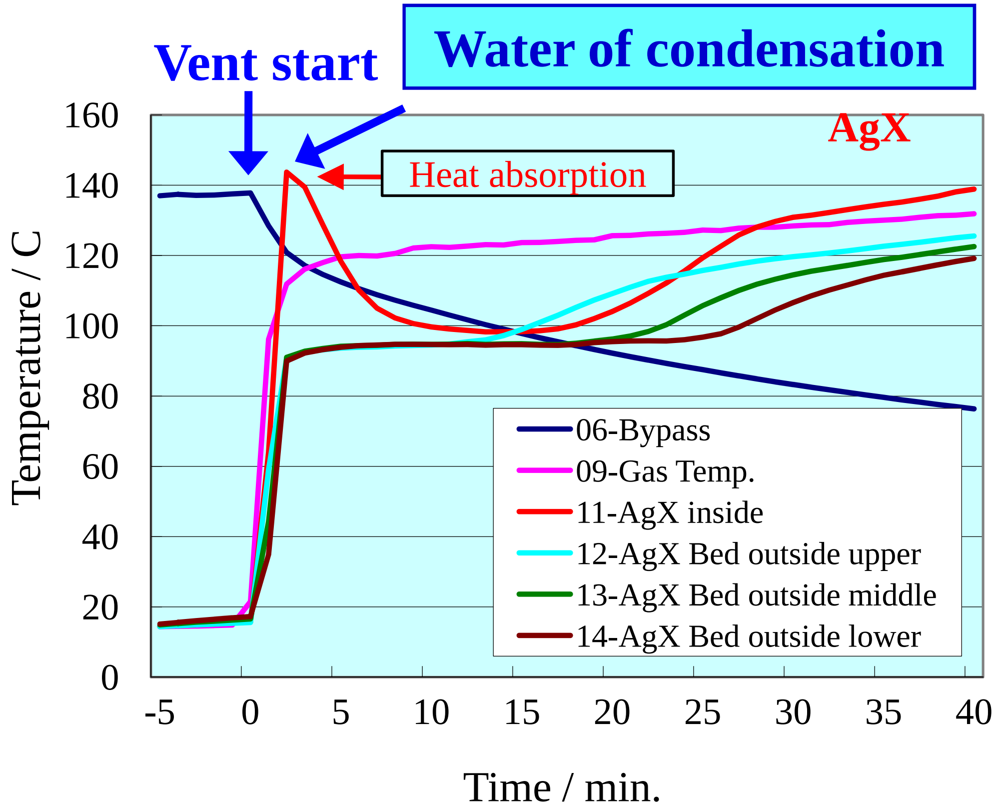


Fig. 6 Dependence of AgX temperature on gas flow time.

Table 7 Gas composition (Vol.%).

Time (min.)	H_2	Air	steam
0-15	2.4	19.0	78.6
15-30	2.0	17.0	81.0
30-60	2.0	16.0	82.0

(At the beginning, Dew point: 93°C)

Table 8 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.

POINT

Venting for 2^{nd}, 3^{rd} times, No Problem

Long-term storage of AgX

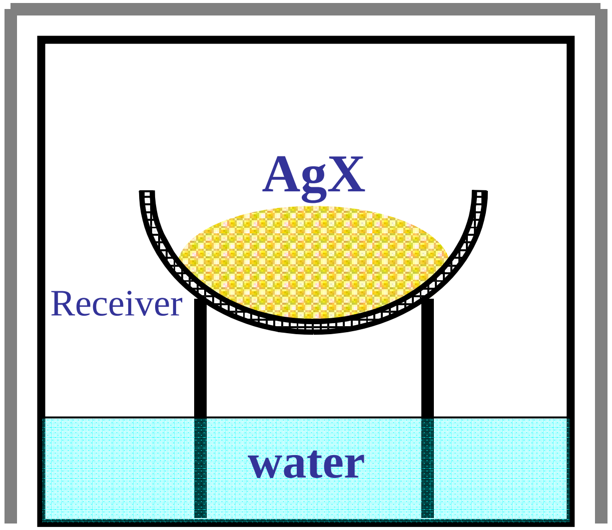


Fig. 7 Schematic diagram of AgX storage.

Table 9 Adsorption efficiencies of CH_3I on AgX that is stored for different periods.

Storage period	105°C DPD:5K	115°C DPD：15K
Initial	＞99.95	＞99.95
After 1.0 year	＞99.95	＞99.95
After 1.5years	＞99.95	＞99.95
After 2.0years	＞99.95	＞99.95
Ongoing	-	-

Test conditions
Gas composition: steam: 100%; Residence time: 0.20 sec.

Storage environment
In a closed container filled with water
(the water is not collected in receiver)
In dark place (no light)
Relative humidity: 100%
In a warehouse
No air-condition

Good adsorption performance can be maintained after AgX is stored at high humidity over 2.0 years

AgX Features

(1) High adsorption efficiency of organic iodine under the harsh conditions.

(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 even if residence time is as short as 0.16 sec.

- a compacted filter can be designed.

(4) Hydrogen removal.- reduce the risk of explosion in an accident.

(5) Good adsorption performance even if water vapor condensation happens.

- AgX is reliable in removing radioactive iodine at the beginning of venting

(6) Adsorption mechanism: chemisorption-irreversible process. Radioactive iodine will be permanently retained on AgX adsorbent

(7) long-term storage at high humidity.

(8) Long product life cycle-shorten exchange period of filter

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

5. Applications of AgX

AgX Filter for Nuclear facility

Vent systems		Reactor containment vessel (RCV)		Other facilities			
Wet system installed in subsequent stage	**Dry system** Combined with metal filter	**SGTS** Boiling Water Reactor (BWR)	**Annulus** Pressurized Water Reactor (PWR)	**Emergency response room** Air-condition filter	**Central control room** Air-condition filter	**Reprocessing plants** Air-condition filter	**Fuel handling plants and stores** Air-condition filter

Filter can be designed according to the processing volume and gas conditions, as well as decay heat.

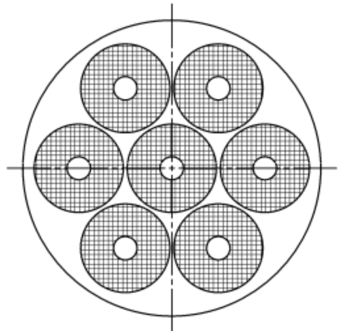
To substitute for doped-activated carbon.

It is smaller than that of charcoal filter.

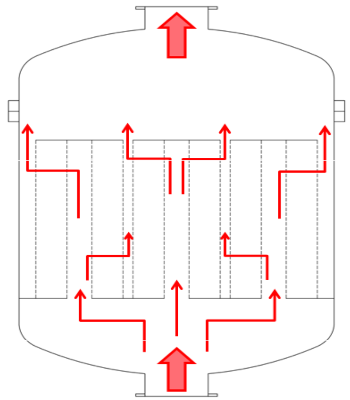
High efficiency particulate air (HEPA) filters and metal filters are already being used. If AgX filters are used alongside, safety will be greatly improved in the event of an emergency.

AgX filter can be designed according to the required specification.

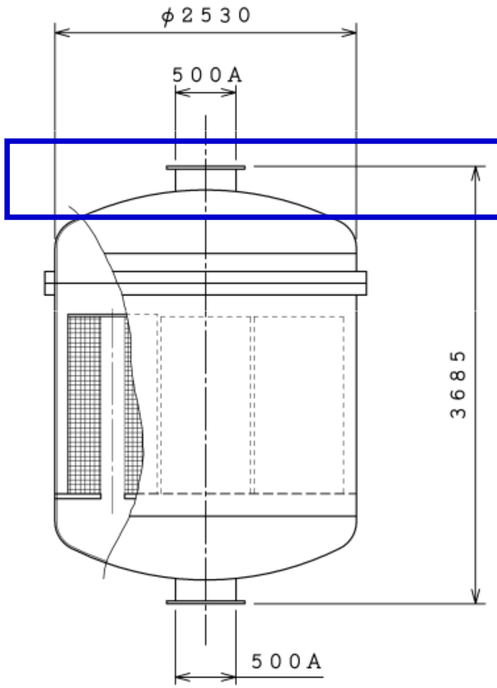
AgX Filter Unit



(a)



(c)



(b)

Fig. 8 Diagrams of AgX filter unit.
(a) Top view; (b) Front view and dimensions; (c) Flow path

Table 10 Standard Specifications of AgX Filter Used in WET System

Flow Rate	25,000 m^3/hr
Max. Operating Pressure	350 kPa
Max. Operating Temperature	200 °C
Max. Pressure Loss	5 kPa
D F	> 100
Applied Standard	JSME, ASME
Seismic Class	S s (Japan Special Criteria)
Material	SUS316L
Mass (Approx.)	15 t

Application to Vent Systems

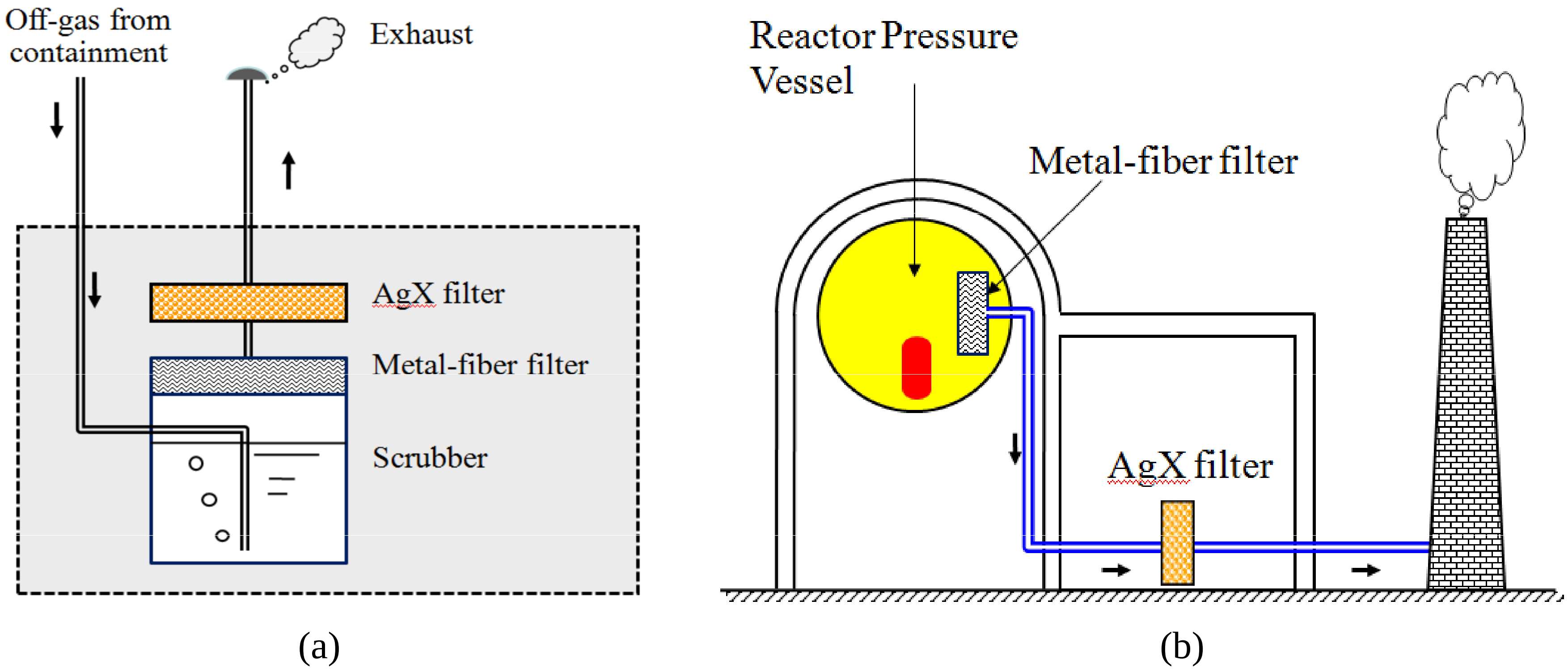
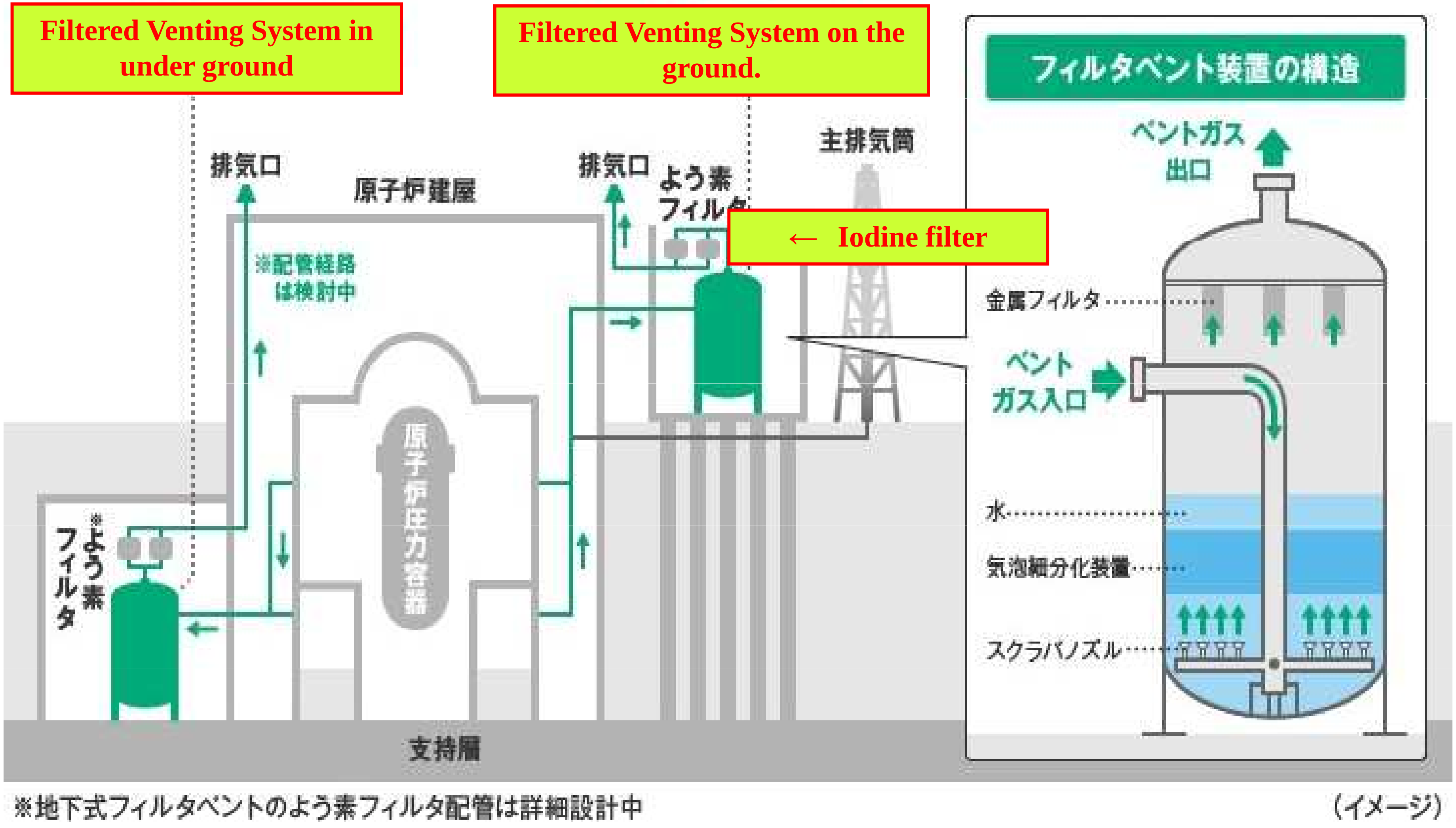
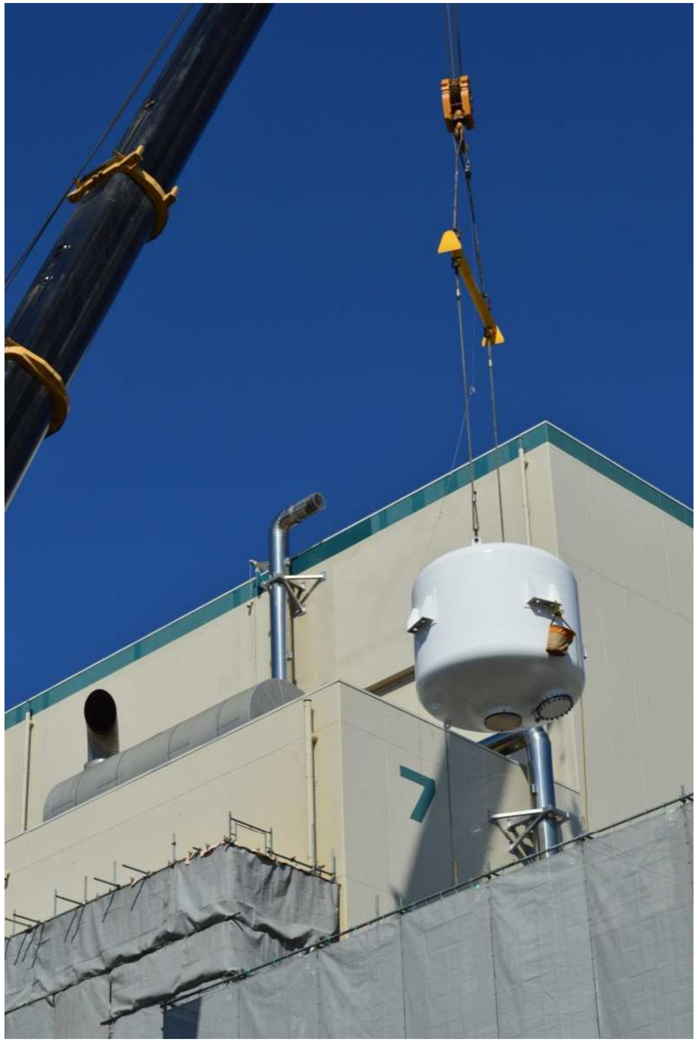


Fig. 9 Application examples of AgX filter. (a) WET-system; (b) DRY-system.

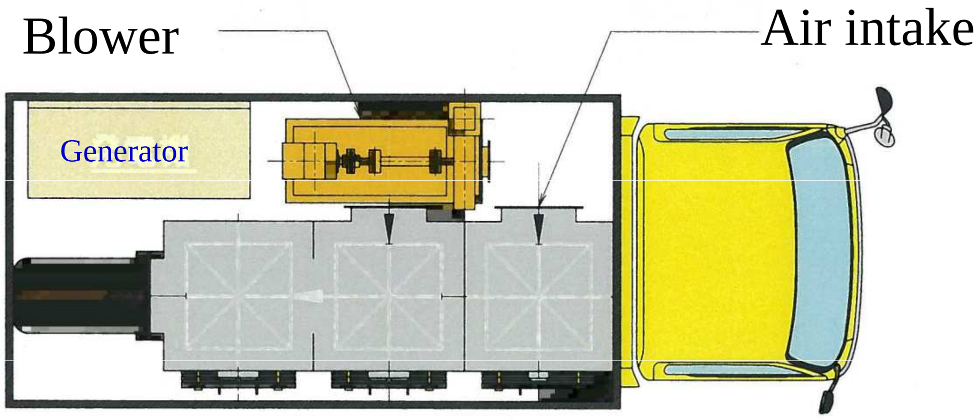
TEPCO Filtered Venting System （Published information from TEPCO）



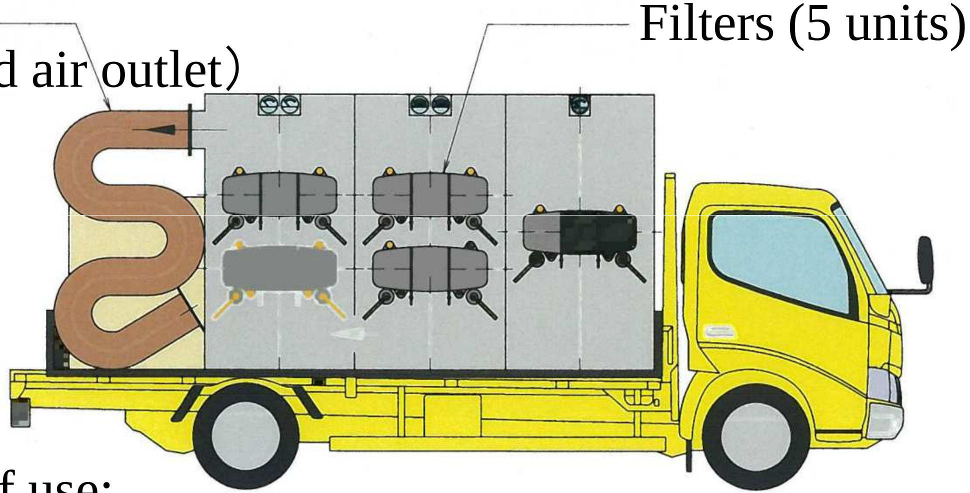
TEPCO AgX Filter (Iodine Filter)（Published information from TEPCO）



6. Mobile type air cleaning system 1000m³/h



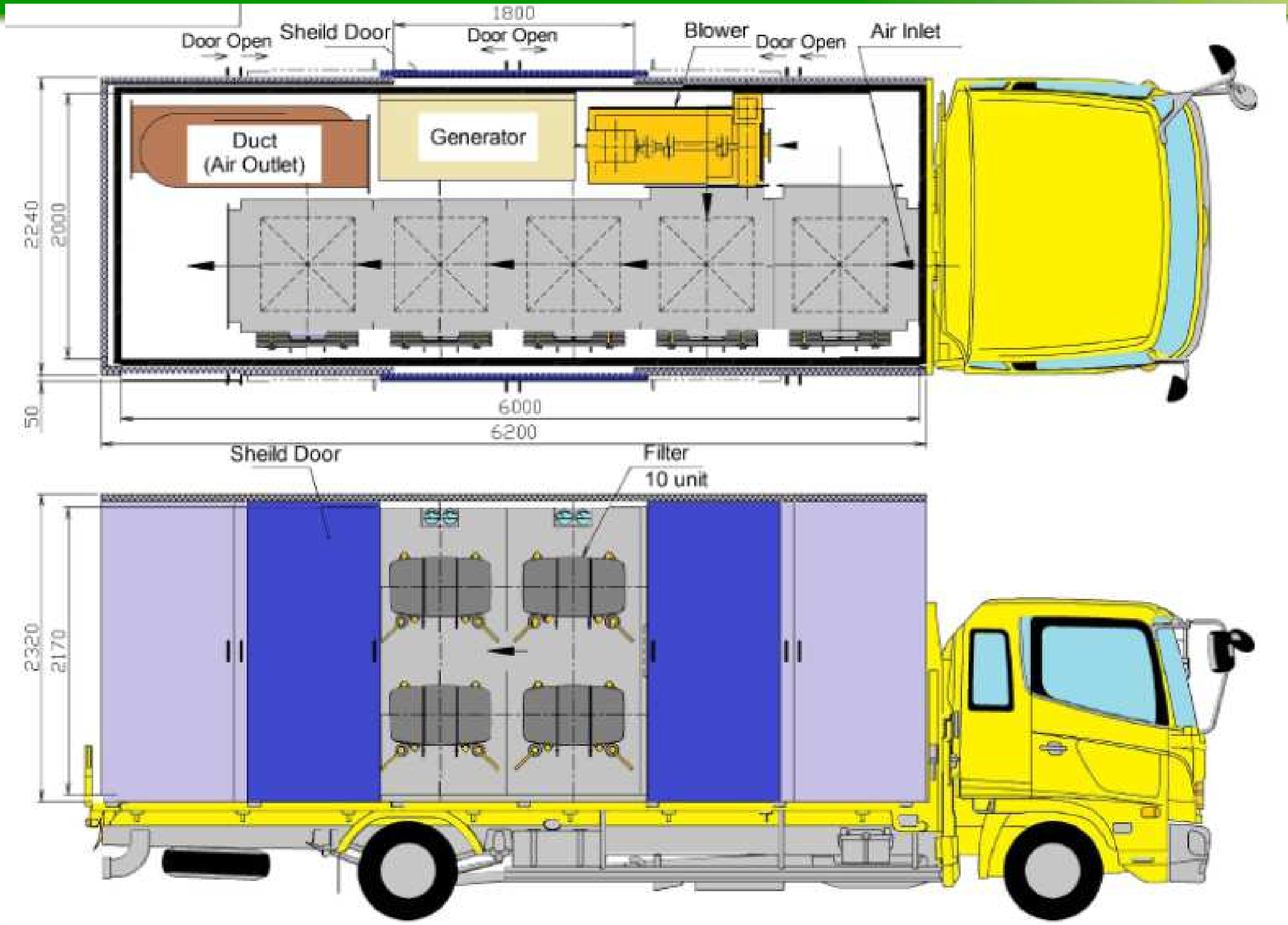
1000 m³/hour
e.g. 2 ton truck



Prefilter
HAPA
Metal fiber
AgX
etc.

Example of use;
Back-up air conditioning for central control room, emergency countermeasure room. Hospital and emergency evacuation area at accident. Off-site center.

Mobile type air cleaning system 2000m^3/h



2000 m^3/hour
e.g. 4 ton truck

With Pb shield

Prefilter
HAPA
Metal fiber
AgX
etc.

Example of use;
Back-up air conditioning for central control room, emergency countermeasure room. Hospital and emergency evacuation area at accident. Off-site center.

6. Exploration of New Adsorbents-AgR

Exploration of New Adsorbents-AgR

AgR Features

1. Low silver content : 10~11 wt % (Dry base)
2. High adsorption efficiency of methyl iodide
3. Weak hydrogen reactivity
   at 150 °C, no catalytic reaction with H_2 is observed
4. Strong hardness
   10 N/pellet (φ1.4mm; L1~3 mm)
5. **AgR (AgX) is very stable in water (Ag^+ is not observed)**

Table 11 Adsorption efficiencies of CH_3I on AgR at various DPDs. These evaluations were performed by TÜV SÜD. Gas composition is steam/air=95/5 .

Residence time (sec.)	DPD 0K (99°C)	DPD 2K (101°C)	DPD 5K (104°C)	DPD 10K (109°C)
0.16	97.68	99.21	99.45	99.83
0.24	99.54	99.89	99.934	99.979
0.32	99.924	99.985	99.994	99.998

Good adsorption performance even 0K and 2K

Evaluation of AgR at the Beginning of Venting

Temp. of venting gas: 120 ℃
Water content in AgR: ~ 4%

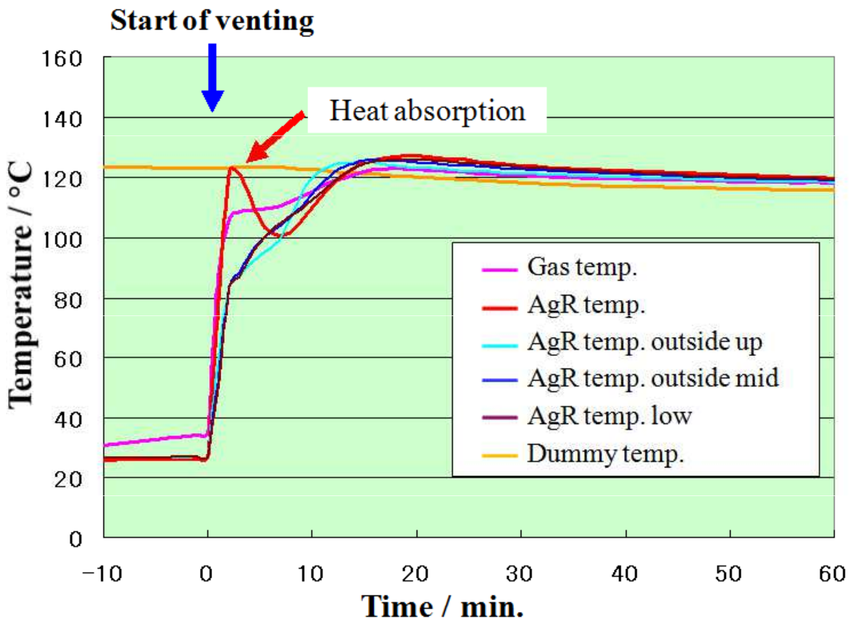


Fig. Dependence of AgR temperature on gas flow time.

Table 14 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. These evaluations were performed by Rasa Industries, Ltd.

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

N_2 is used as a substitute for CO_2 and CO. * Detection limit.

AgR shows high adsorption efficiencies of organic iodine even if 10% H_2 exists in atmosphere

Adsorption Efficiency of CH_3I under the Harsh Conditions

Table 12 Relationships between absorption efficiency of **CH_3I** and bed depth at the high temperature, relative humidity (RH) and pressure. The evaluation was performed by NUCON International Inc.. Radioiodine: CH_3I (I-131) of 1.75 mg/m^3

Absolute pressure Relative humidity	**P=399 kPa, RH=95 %**		
Residence T (Bed depth) Temp.	0.125 sec. (50.8 mm)	0.187 sec. (76.2 mm)	0.250 sec. (101.6 mm)
110 (ºC)	99.569 %	99.994 %	>99.999 %
120 (ºC)	99.351 %	99.944 %	>99.999 %
130 (ºC)	98.998 %	99.912 %	> 99.999 %

AgR exhibits the high adsorption efficiency under the harsh conditions (high T, high P and high RH)

Adsorption Efficiency of Iodine under the Harsh Conditions

Table 13 Relationships between absorption efficiency of **elemental iodine** and bed depth at the high temperature, relative humidity and pressure. The evaluation was performed by NUCON International Inc. Radioiodine: I-131 of 1.75 mg/m^3.

Absolute pressure Relative humidity	**P=399 kPa** **RH=95 %**		
Residence T (Bed depth) Temp.	0.125 sec. (50.8 mm)	0.187 sec. (76.2 mm)	0.250 sec. (101.6 mm)
110 (ºC)	99.998 %	> 99.999 %	>99.999 %
130 (ºC)	> 99.999 %	> 99.999 %	> 99.999 %

AgR exhibits the high adsorption efficiency under the harsh conditions (high T, high P and high RH)

7. Conclusions and future work

Conclusions

1. Rasa-AgX and AgR show excellent adsorption characteristics of radioiodine (CH_3I and elemental iodine) under the venting conditions. They are efficient even if the venting is operated for 2nd and 3rd times.
2. Both of AgX and AgR are very stable in water.
3. AgR shows its effectiveness even in the atmosphere of 10% H_2.

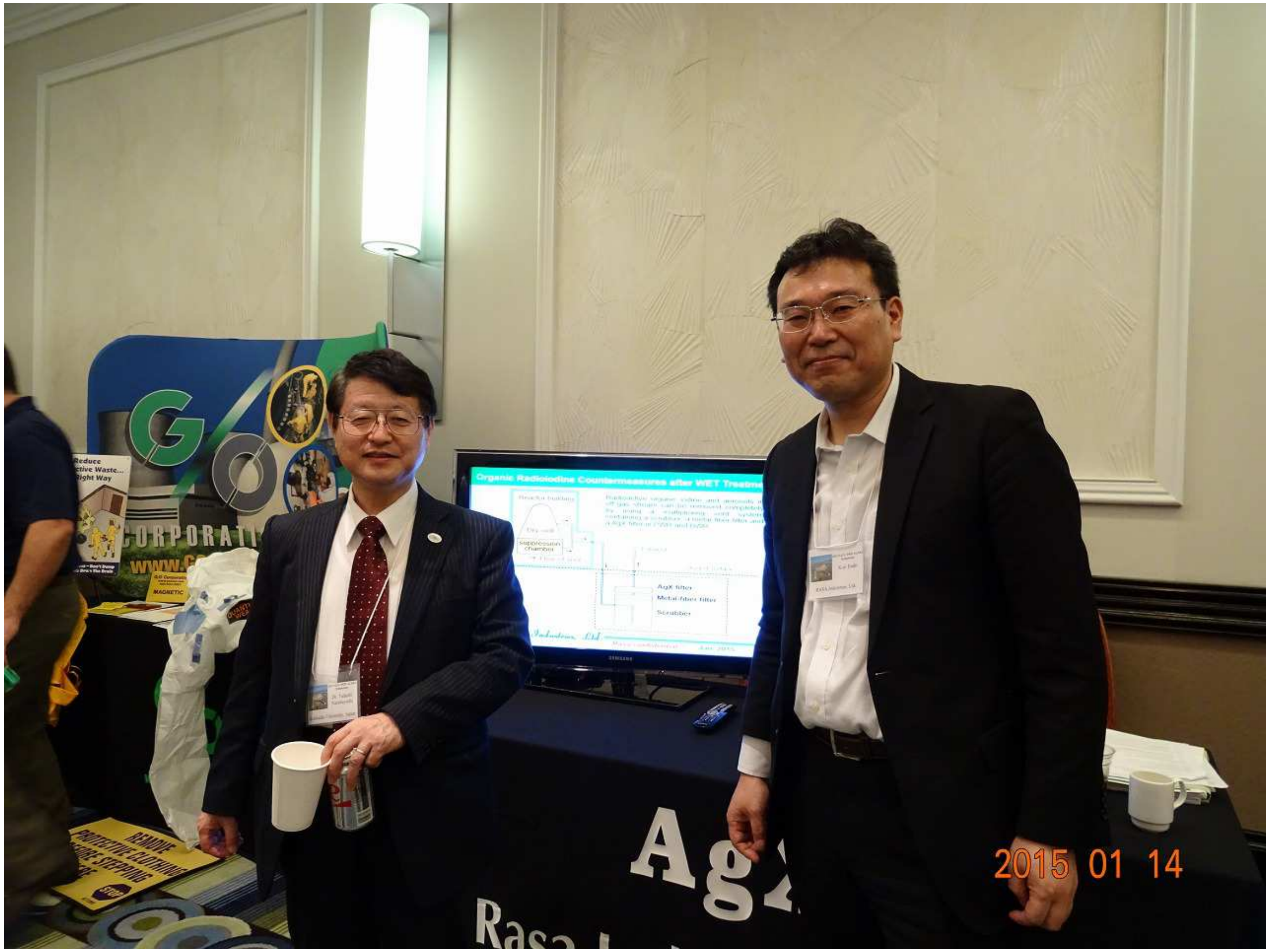
Future work

1. We are devoting to improve our product quality and service.
2. We are exploring the new adsorbents and their applications. Some results have shown good adsorption performance

We are looking forward to contributing our AgX and AgR to more nuclear facilities

2014 International *ISOE* ALARA Symposium

2015 International *ISOE* ALARA Symposium



We are looking forward to cooperating with you

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