

Newly Developed Gaseous Decontamination Technology

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ABSTRACT

Decontamination and volume reduction of the radioactive wastes generated by atomic power plants, nuclear fuel reprocessing plants and nuclear research institutes has proven to be extremely difficult.

With regard to two cases of heavy metals and hydrogen isotope (tritium), two kinds of newly developed gas-phase decontamination technology based on gaseous reactions are introduced. One is based on utilizing volatile properties of carbonyl compounds and fluoric compounds of radioactive transition elements and actinides (corrosion products: CP, fission products: FP, trans-uranium: TRUs), and another is based on the treatment by ozone gas to decontaminate the tritiated wastes.

If gas-phase decontamination technology will be practicable, it will not only be convenient, but economically advantageous as well, since it is currently very difficult to decontaminate and treat the large volume of nuclear wastes; especially non-incinerable radioactive wastes.

I. Gaseous Decontamination for radioactive heavy metals¹⁾

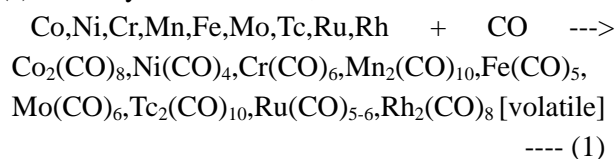
I-1. Introduction

The purpose of this study is to investigate the feasibility of simultaneous decontamination by means of gaseous reactions. Many radioactive transition elements (e.g. cobalt-60, cobalt-58, nickel-63, manganese-54, chromium-51, etc) as well as other neutron irradiated products and fission products (e.g. molybdenum, technetium, ruthenium, etc.), and actinides (uranium, neptunium, plutonium, etc.) are troublesome at nuclear sites and waste management facilities. The carbonyl and fluoric

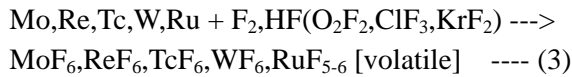
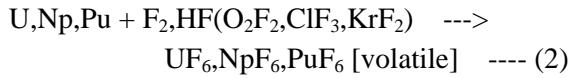
compounds of radioactive transition elements are probably volatile. Therefore, the objective of gas-phase decontamination is to use CO gas for carbonylation and fluoric gases for fluorination, in order to convert nonvolatile radioactive transition elements and actinides to volatile chemical species, such that evaporation is possible. Carbonyl compounds of normal transition elements have volatile properties. Some fluoric compounds of FP and TRUs also have volatile properties. Because the carbonyl and fluoric compounds have thermal properties giving them low melting points, low boiling points, and/or sublimation points, many of these compounds can become gaseous or volatile at a lower temperature, such as room temperature. New decontamination technology introduced in this paper is based on the utilization of these volatile properties.

By the reaction of CO gas with transition elements on a material's surface, carbonyl compounds are produced. When radioactive transition elements (e.g. cobalt-60, cobalt-58, nickel-63, manganese-54, chromium-51, molybdenum-99, technetium-99, ruthenium-106, etc.) exist on a material's surface, these radioactive transition elements can be evaporated as gaseous forms by converting them to their carbonyl compounds. In the case of actinides, volatile fluoric compounds are formed by reacting them with fluoric gases (e.g. F₂, HF, O₂F₂, ClF₃, BrF₅, etc.). The related chemical reactions utilized are indicated by Eqs. (1)-(3);

(a) Carbonylation reaction;



(b) Fluorination reaction;



If both carbonylation and fluorination reactions occur at the same time, the gaseous codecontamination of many troublesome CP, FP, and TRUs may be possible. The concept of codecontamination by using carbonylation and fluorination reactions is shown in Fig. 1.

1-2. Treatments to Generate Gaseous Compounds

The chemical-forms of generally troublesome nuclides after carbonylation and fluorination were predicted in Table-1. Radioactive transition elements of CP and FP appear either as carbonyl forms or fluoric forms, and actinides (TRUs) take on gaseous or volatile fluoric forms. However, despite knowing the fundamental chemical behaviors of elements, alkali and alkali earth metal elements (e.g. cesium-134 and -137, strontium-90), rare earth elements (e.g. cerium-144, praseodymium-144, promethium-147, europium-154), and two of the TRUs (americium and curium) could neither be categorized as carbonyl compounds nor fluoric compounds, and remain categorized as "unknown". Furthermore, it was not clear whether or not the carbonyl or fluoric compounds for

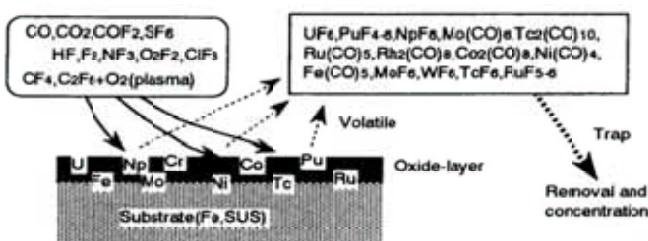


Fig.1 Concept of gas-phase codecontamination technology of corrosion and fission products and TRUs by simultaneous carbonylation and fluorination under conditions of high temperature, high pressure, supercritical fluid, chemical reactive plasma, and /or highly reactive gases.

yttrium-90 and niobium-95, grouped with the radioactive transition elements, were transformed.

Four treatment methods to generate gaseous metal compounds were investigated. The characteristics, differences and assumed reactions of the four treatment methods are described below.

- 1) Method-1: Carbonylation and fluorination reactions under high pressure and high temperature
- 2) Method-2: Promotion of the carbonylation and fluorination reactions utilizing supercritical CO₂ fluid
- 3) Method-3: Carbonylation and fluorination reactions utilizing chemically reactive plasma

In order to decontaminate under the mild conditions without the hard treatment at a high temperature and pressure, the treatment is carried out by using plasma under the conditions of room temperature and reduced pressure to generate the unstable and highly reactive carbonyl and fluoric species. The concept of the chemically reactive plasma treatment is shown in Fig. 2. It is assumed that the chemically reactive species (radical, ion-F, CO) generated by the plasma reaction of Eq. (4) react with the target nuclides to yield the carbonyl and fluoric compounds as shown by Eq. (5);

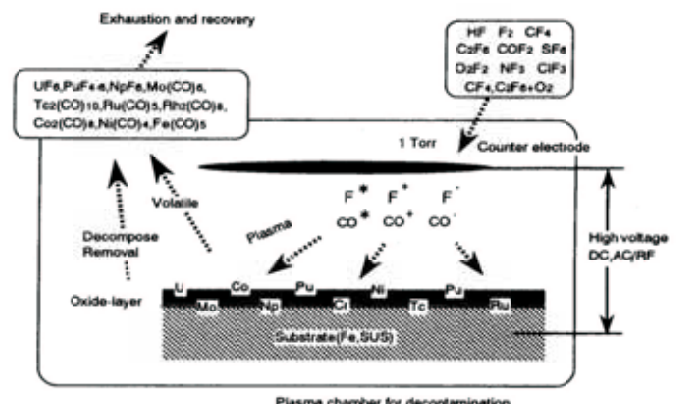


Fig.2 Codecontamination concept of chemically reactive plasma

$F_2/CF_4, C_2F_6/CF_4+O_2$ ---> plasma
 ---> radical, ion-F, CO [F*, F-, F+ & CO*, CO-, CO+] ---- (4)
 radical, ion-F, CO + Co, Ru, U(CP, FP, TRUs)-metal or oxide --->
 $Co_2(CO)_8, Ru(CO)_5, RuF_{5-6}, UF_6$ [volatile] ---- (5)

4) Method-4. Fluorination reaction utilizing highly reactive gas without plasma treatment
 Furthermore, for decontamination under the more simple treatment conditions without using plasma, some fluorine reagents such as $O_2F_2, ClF_3, BrF_5, KrF_2$, etc. which naturally generate the

radical-fluoric species even under the conditions of room temperature and reduced pressure were used. The chemical reaction of the fluorine reagents is predicted as follows;
 $ClF_3, O_2F_2, BrF_5, KrF_2$, etc. + U, Pu, Np, Tc, Ru, etc. ---> $UF_6, PuF_6, NpF_6, TcF_6, RuF_{5-6}$, etc. [volatile] ---- (6)

Carbonyl reagents which can naturally generate radical carbonyl species at ambient temperature have not been known. Therefore, the carbonylation reaction using highly reactive gas was not investigated in this study.

Table 1 Properties of gaseous compounds of primary troublesome nuclides of corrosion and fission products and TRUs

Classification	Nuclide	Half-Life	Primary Generating Nuclear Reaction	Method*	Primary Gaseous Form	
Corrosion products	^{51}Cr	27.7 days	$^{50}Cr(n, \gamma)$	CO	$Cr(CO)_6$	
	^{54}Mn	312 days	$^{56}Fe(d, \alpha)$	CO	$Mn_2(CO)_{10}$	
	^{59}Fe	44.6 days	$^{58}Fe(n, \gamma)$	CO	$Fe(CO)_5$	
	^{58}Co	70.8 days	$^{58}Ni(n, p)$	CO	$Co_2(CO)_8$	
	^{60}Co	5.27 yr	$^{59}Co(n, \gamma)$	CO	$Co_2(CO)_8$	
	^{63}Ni	100 yr	$^{62}Ni(n, \gamma)$	CO	$Ni(CO)_4$	
	^{65}Zn	244.1 days	$^{64}Zn(n, \gamma)$	CO	$Zn(CO)_5$	
	^{90}Sr	28.8 yr	$U(n, f)$	unk	?	
	^{134}Cs	2.06 yr	$^{133}Cs(n, \gamma)$	unk	?	
	^{137}Cs	30.17 yr	$U(n, f)$	unk	?	
Fission products	^{90}Sr	28.8 yr	$U(n, f)$	unk	?	
	^{90}Y	64.1 h	$^{90}Sr \rightarrow$	unk	?	
	^{95}Nb	35.0 days	$^{95}Zr \rightarrow$	unk	?	
	^{99}Tc	$2.1E+5$ yr ^b	$U(n, f) \text{ } ^{99}Mo / \text{ } ^{99m}Tc \rightarrow$	CO/F	$Tc_2(CO)_{10} / TcF_6$	
	^{106}Ru	367 days	$U(n, f)$	CO/F	$Ru(CO)_5 / RuF_{5-6}$	
	^{134}Cs	2.06 yr	$^{133}Cs(n, \gamma)$	unk	?	
	^{137}Cs	30.17 yr	$U(n, f)$	unk	?	
	^{144}Ce	284 days	$U(n, f)$	unk	?	
	^{144}Pr	17.3 min	$^{144}Ce \rightarrow$	unk	?	
	^{147}Pm	2.62 yr	$U(n, f)$	unk	?	
	^{154}Eu	8.5 yr	$^{153}Eu(n, \gamma)$	unk	?	
	TRUs	^{235}U	$7.04E+8$ yr	Natural	F	UF_6
		^{238}U	$4.47E+9$ yr	Natural	F	UF_6
^{239}Np		2.35 days	$^{239}U \rightarrow$	F	NpF_6	
^{238}Pu		87.74 yr	$^{238}Np \rightarrow$	F	PuF_6	
^{239}Pu		$2.41E+4$ yr	$^{239}Np \rightarrow$	F	PuF_6	
^{240}Pu		$6.57E+3$ yr	$^{239}Pu(n, \gamma)$	F	PuF_6	
^{241}Pu		14.4 yr	$^{240}Pu(n, \gamma)$	F	PuF_6	
^{242}Pu		$3.78E+5$ yr	$^{241}Pu(n, \gamma)$	F	PuF_6	
^{241}Am		433 yr	$^{241}Pu \rightarrow$	unk	?	
^{242}Am		16.01 h	$^{241}Am(n, \gamma)$	unk	?	
^{243}Am		$7.95E+3$ yr	$^{242}Am(n, \gamma)$	unk	?	
^{242}Cm		162.8 days	$^{242}Am \rightarrow$	unk	?	
^{244}Cm		18.11 yr	$^{244}Am \rightarrow$	unk	?	

*Conversion method to gaseous form by this technology (CO: by carbonylation, F: by fluorination, and unk: unknown).

^bRead as 7.1×10^5 yr

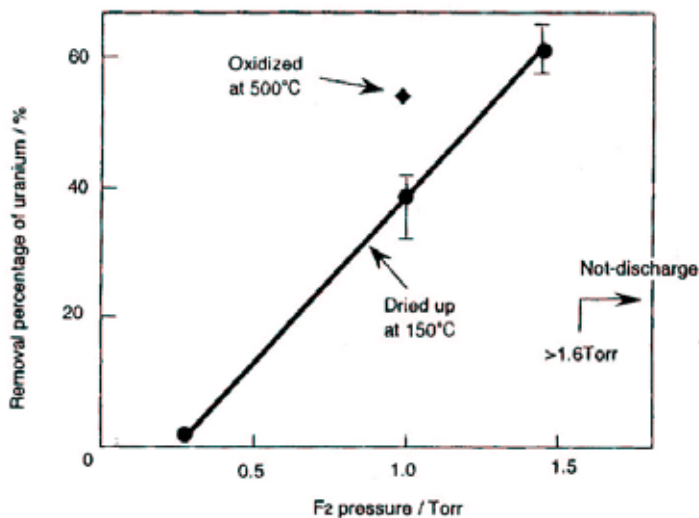


Fig.3 Effect of F₂ gas pressure on the removal efficiency of U by plasma treatment.

I-3. Gaseous Decontamination utilizing the chemically reactive plasma and the fluorination reaction utilizing highly reactive gas

In this paper, the outline of carbonylation and fluorination reactions utilizing chemically reactive plasma (as Method-3), and the fluorination reaction utilizing highly reactive gas without plasma treatment (as Method-4) are shown.

I-3.1 Chemically Reactive Plasma (as Method-3)

Tests were performed varying the pressure of reaction gases, treatment time, the kinds of gases, the pretreatment conditions of mounting-sample materials, and the type of nuclides (cobalt-60 and

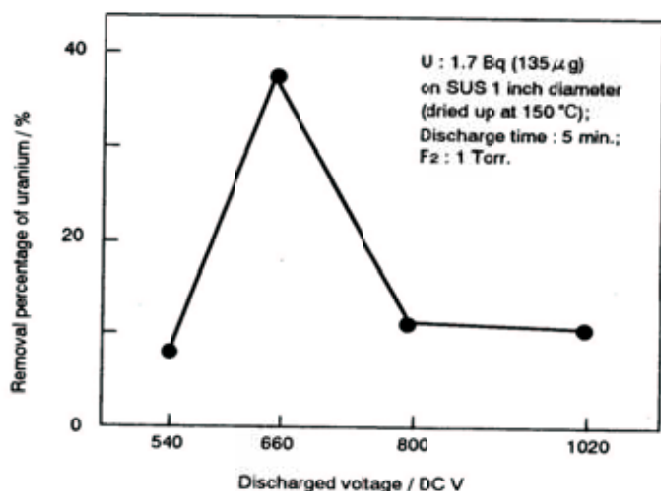


Fig.4 Removal efficiency of U compared with voltage discharged by plasma treatment.

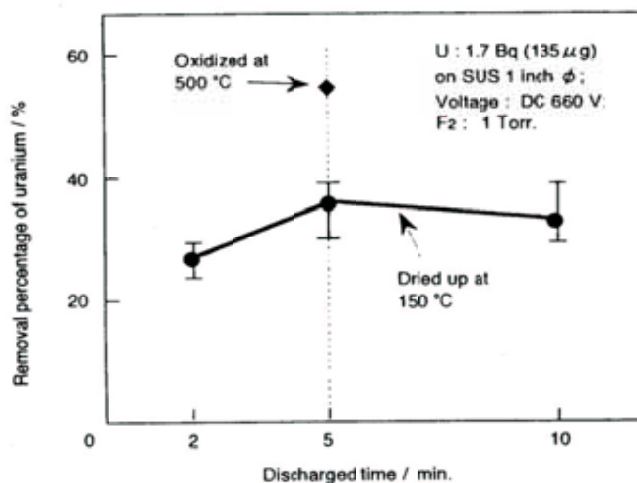


Fig.5 Removal efficiency of U compared with treatment time of plasma

uranium).

The results of the feasibility tests are shown in Figs. 3-5, indicating that uranium was removed by plasma treatment using F₂ gas. The removal efficiency of uranium was sensitive to F₂ pressure (Fig. 3), and also depended on the discharged voltage (Fig. 4). The effect of the treatment time (discharged time) was not so large for any period exceeding 2 min. (Fig. 5). Uranium was decontaminated with a high efficiency for a short time, and that fluorination-utilized plasma treatment is feasible in decontaminating TRUs and some FPs.

Next, using non-toxic gases, codecontamination of two or more elements by simultaneous carbonyl and fluoric reactions under the plasma treatment was investigated. The CF₄ and O₂ gas mixture was used as the plasma gas-reactant. Fig. 6 shows the result on codecontamination of radioactive cobalt (Co-60: 12.5 kBq) and uranium (2.1 Bq). Taking note of Fig. 6, the removal efficiency of uranium was high at 100 % with a flow rate of 50 cc/min., while that of cobalt-60 was comparably high (about 80 %). Thus, it was confirmed that the plasma treatment of carbonylation and fluorination utilizing non-toxic gases is feasible for the simultaneous decontamination of many nuclides (CP, FP and TRUs). The effect of the mixed gas plasma of CF₄

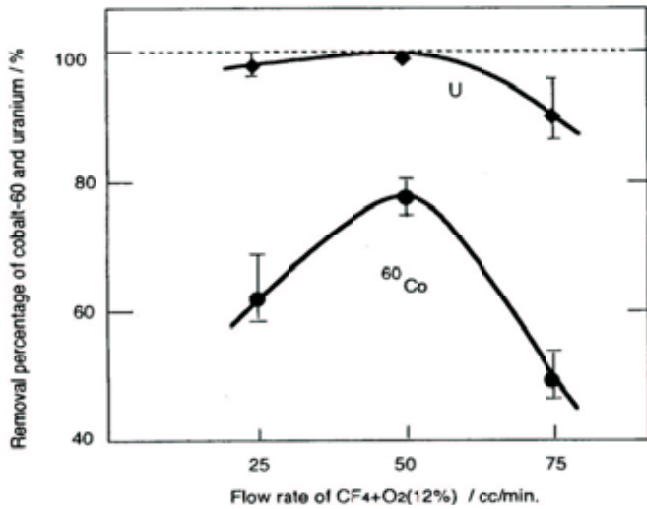


Fig.6 Removal efficiency of ⁶⁰Co and U compared with flow rate of plasma gas of CF₄ + O₂(12%)

and O₂ to remove the thick uranium layer (U₃O₈) on stainless steel is shown in Fig. 7, which shows pictures before treatment and after one-time short plasma treatment. As shown, the thick uranium layer was removed by the treatment of chemically-reactive plasma using the gas-mixture. The gaseous uranium fluoride and excess unreacted fluorine gas were completely trapped by the Halogen-filter. It was concluded, therefore, that even in the case of thick contamination, it is possible to remove the contaminated surface layer.

Furthermore, plasma treatments using other non-toxic gases such as CO₂+H₂, CH₄+O₂ and CF₄ only were investigated to generate reactive

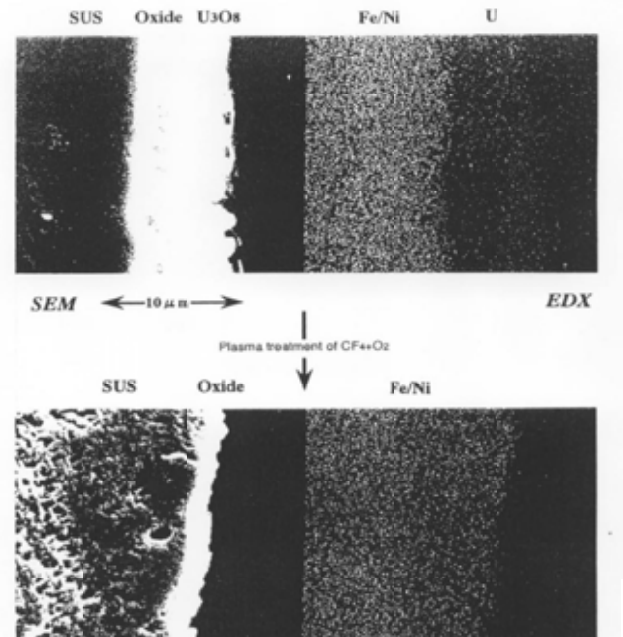


Fig.7 Removal of thick U layer(U₃O₈) by plasma of CF₄ + O₂(cross sections of SUS304 surface).

carbonyl and fluoric species. Tests using cobalt-60 and uranium were conducted to examine the pretreatment effect of H₂ gas for reduction the chemical forms of target nuclides, thereby reducing the valency of the uranium. The results are shown in Table-2. Judging from the removal data of cobalt-60 in Table-2, the plasma treatment using a mixture of gas [containing carbon but not fluorine: e.g. CH₄, CO₂, etc.] and oxygen has the ability to generate the carbonyl species. Also, only CF₄ has the ability to remove cobalt-60 by itself from the

Table 2 Removal efficiency of ⁶⁰Co and U by mixed-gas plasma

Gas	Treatment*	⁶⁰ Co Removed (%)	U Removed (%)
CF ₄ + O ₂ (12%)	Oxidized, pretreat by H ₂ discharge	76.3	98.2
	Dried up, pretreat by H ₂ discharge	78.0	99.3
	Oxidized, pretreat by H ₂ discharge	67.2	93.0
	Oxidized, without pretreatment of H ₂ discharge	57.4	93.1
CO ₂ + H ₂	H ₂ 50%, dried up	2.4	---
	H ₂ 10%, dried up	2.9	---
CH ₄ + O ₂	O ₂ 12%, dried up	13.5	---
	O ₂ 24%, dried up	7.1	---
CF ₄	Oxidized, without pretreatment of H ₂ discharge	64.8	93.0

*The conditions were as follows: SUS sample contaminated with U and ⁶⁰Co: U, 2.1 Bq (169 μg) and ⁶⁰Co, 1.26 kBq; sample treated at 150°C (some samples): 500°C × 1 h; gas flow rate: 44 to 50 cm³/min; pressure of plasma gas: 0.9 to 1.6 Torr; discharge conditions: 660 to 720 V(dc), 20 to 70 W.

*Sample, etc.

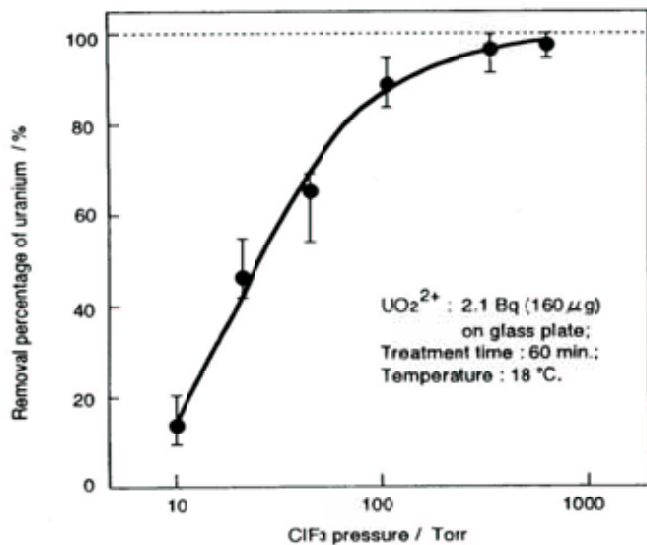


Fig.8 Effect of ClF₃ pressure on the removal efficiency of U.

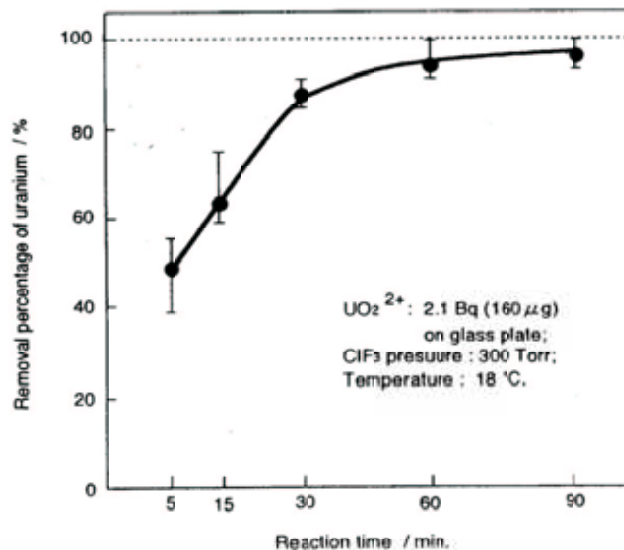
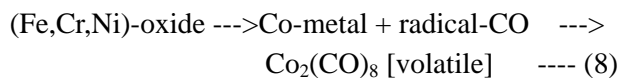
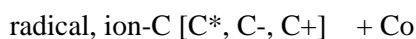
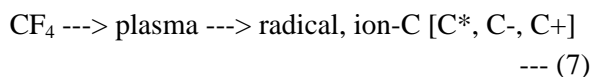


Fig.9 Effect of reaction time on the efficiency of U with ClF₃

oxidized metal surface. As the most likely reason, cobalt-60 pretreated by oxidation might be attacked by a radical carbon atom generated by the plasma treatment of CF₄; the reaction between radical carbon atoms and oxygen from the oxide layer or from the cobalt compound on the pretreated stainless steel sample. Eqs. (7)-(8) indicate the presumptive behavior. The effects of the H₂ pretreatment, on the other hand, was not as obvious.



I-3.2 Fluorination Reaction Utilizing Highly Reactive Gas (as Method-4)

In this case, only the fluorine reaction was investigated, since chemical reagents which can naturally generate radical carbonyl species at ambient temperature

have not been known.

To determine the feasibility of decontamination at ambient temperature by a highly chemical fluorine reaction, tests using glass-plate as the sample for pre-mounted uranium were conducted in the varying conditions of pressure and reaction time with the ClF₃ treatment. Increasing the pressure of ClF₃ effected a gradually higher removal efficiency of uranium, as shown in Fig. 8. The removal efficiency shows a linear relationship with pressures in the range of 10 to 100 Torr; at a pressure of over 100 Torr, removal efficiency was more than 90 %. The effect of treatment time also has a linear relationship with removal efficiency for the time between 5 and 30 min. While the slope of this relationship tapers off for the reaction time between 30 and 90 min., removal efficiency continues to increase during this period, to over 95 % (Fig. 9). From the results, it was verified that a

Table 3 Effect of chemical forms of U on removal efficiency.

Source of U ^a	Mounted Activity	Pretreatment	Assumed Chemical Form of U	Percentage of Removal (%)
UO ₂ ²⁺	2.1 Bq 169 μg (as U)	Dried up at 110 to 120°C for 2 to 3 h Heated at 500°C for 1 h in air	UO ₂ (NO ₃) ₂	32.0 ± 4.7
			U ₃ O ₈	50.7 ± 6.2

^aThe UO₂²⁺ was mounted on stainless steel (SUS304).

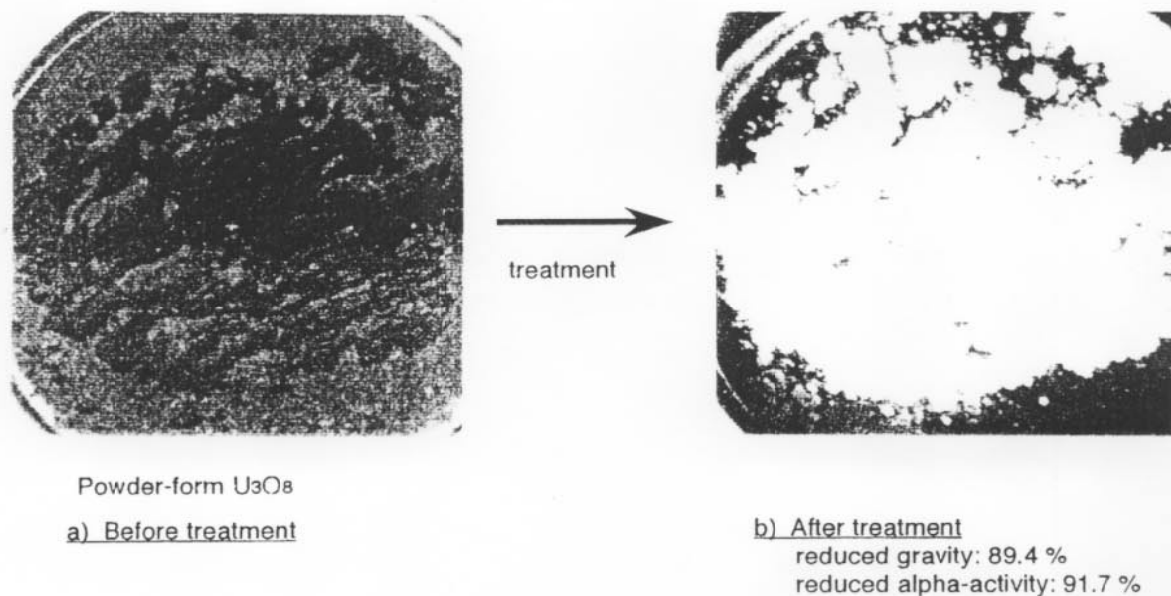


Fig.10 Treatment of powder-form U₃O₈ with ClF₃ at 400 Torr and 18 °C for 30min. This treatment was repeated twice

fluoric reaction at ambient temperature can be attained for the purpose of removing the solid-deposits of uranium by converting them to gaseous uranium compounds.

To observe the effects of differing chemical formations of uranium (U₃O₈, UO₂, or other ?), stainless steel samples with pre-mounted uranium were dried up at 150 °C, and heated in air for 1 h at 500 °C. Results showed that the chemical form of uranium might be transformed into U₃O₈ by the pretreatment at 500 °C. As shown in Table-3, the removal efficiency may be indeed affected by the valency of uranium.

As showing in Fig. 10, fluorination reactivity of ClF₃ toward powder-form U₃O₈ accumulated was reconfirmed. By the treatment using 0.105 g (0.124 mmol) of U₃O₈, the decreased ratio of alpha activity and gravity of U₃O₈ after the reaction were observed to be nearly identical each other. By ClF₃ treatment at 400 Torr for 30 min., and twice again at room temperature (18 °C), 90 % of U₃O₈ was removed in gaseous form, and dark green powder-form U₃O₈ became white color. The gaseous fluoric compound and unreacted excess ClF₃ were completely trapped by the

Table 4 Technical comparison of decontamination by wet method and proposed dry method.

Item	Dry Method Utilizing Gaseous Reaction	Wet Method
Equipment for decontamination	Small, decontaminatable in situ	Large and many by scrapping equipment and liquid waste
Process of decontamination	Simple process, easy handling and control, possible in short period	Complex process; needs a long period
Secondary waste	Small	Large secondary and final waste
Final waste	Small space by highly decontaminated efficiency	
Decontaminable nuclides	Corrosion and fission products and TRUs except alkali metal and alkali earth metal elements	All (corrosion and fission products and TRUs)

Halogen-filter.

I-4. Applications

The primary characteristics of gas-phase decontamination and conventional wet-methods are shown in Table-4. The gas-phase decontamination technology has many advantages over conventional wet-methods; in particular, its simple control processes and small secondary waste.

Using the gas-phase treatment concurrently with existing chemical, mechanical, and physical treatments, high-efficiency waste management will be attained in the not-so-distant future. Gas-phase decontamination will become a practical technology as soon as optimum treatment methods and conditions have been determined. This proposed decontamination technology based on gaseous reaction has the ability and potential to drastically decrease the large volumes of the large volumes of wastes created each year or non-incinerable radioactive wastes, which include burned-ash, many kinds of used-metals, and discarded equipment.

I-5. Conclusion

In regard to a surface contamination, the newly developed concept and technology of gas-phase decontamination, which is an advanced waste management technology, was proposed.

The results obtained in this study are summarized below;

- (1) By the treatment of CO gas under a high temperature and pressure using non-radioactive elements and radioactive nuclides of transition elements, they were evaporated with high efficiency as gaseous forms.
- (2) By the simultaneous carbonylation and fluorination reactions, the co-decontamination of cobalt-60, ruthenium-103 and uranium was verified.
- (3) In the case of stainless steel coated by a oxide layer containing radioactive nuclides, the removal treatment of the oxide layer by utilizing the pretreatment with chemically reactive supercritical CO₂ fluid promoted the carbonylation and fluorination reactions. It is anticipated that the treatment by chemically reactive supercritical treatment will be practical and applicable in not only decontamination of wastes but also many other fields.
- (4) From the results of tests to determine the ability to generate radical fluoric species by the plasma treatment of fluorine gas, uranium was removed with high efficiency. In the case of generating carbonyl and fluoric species using a non-toxic gas mixture, it was verified that uranium and cobalt-60 were removed simultaneously with the high removal efficiencies.

Table 5 Outline of characteristics and availability of developed gas-phase decontamination technology.

Removable contamination	Surface contamination; simultaneous use of supercritical fluid or plasma in the cases of deep or diffused contamination
Method	Perfect gas-phase chemical decontamination; utilizing carbonyl and fluoric reactions
Kinds of wastes	Nonincinerable waste, used metal, ash; used reactor (for decommissioning), etc.
Removable radioactive nuclides	Corrosion products, fission products, and TRUs
Advantages of decontamination technology	Removable contamination under the scrapped or unscrapped states High removal efficiency Small secondary waste Simple process Isolation or separation of target nuclides High decreasing waste (volume and weight) Possibility of reusing or reutilizing waste materials

(5) Finally, from the results of the test to reconfirm the feasibility of decontamination using highly chemical fluorine reaction without the use of plasma, ClF_3 at ambient temperature has the potential to remove the solid-deposits of uranium.

By the experimental results using non-radioactive and radioactive nuclides indicated above, the feasibility of this new idea was asserted. The outline of characteristics and capabilities of the newly-developed technology of gas-phase decontamination technology is shown in Table-5.

II. Dry Decontamination for Tritiated Wastes²⁾

II-1. Introduction

Until now, as the decontamination of tritiated contaminants, swiping method using wet paper or cloth, brushing or polishing surface contaminated, heating method to remove by evaporation, blowing by highly compressed water, blowing by hot water vapor, and others have been developed and a part of them is being used in practice. However, the use of them has sometimes caused many problems such as the generation of large secondary wastes, high cost, long working

time, dangerous working and others. The development of an effective and useful decontamination technology has been expected because the satisfying methods for tritium decontamination have not been formerly. By the reason, in the nuclear fields, it is an important subject to develop an effective and useful decontamination technology for tritiated contaminants. The aim of this study is to develop an available decontamination technology by applying gaseous method using ozone gas.

II-2. Experiment

In order to develop a gaseous decontamination technology for tritium, the tests of ozone gas treatment were performed using tritiated contaminants. For the tests, the specimen sheets sized 20mm x 20mm x 1mm of non-treated (NT) SS-304 rolled, electrolytic polished (EP) SS-304 rolled and aluminum (A-5052) contaminated by tritium were prepared. After cleaning the specimens by heating in a vacuum, they were contaminated by exposure to tritium gas (T_2) of purity 40.4 % and pressure of 2.5 Torr at 300 K for 6 hours.

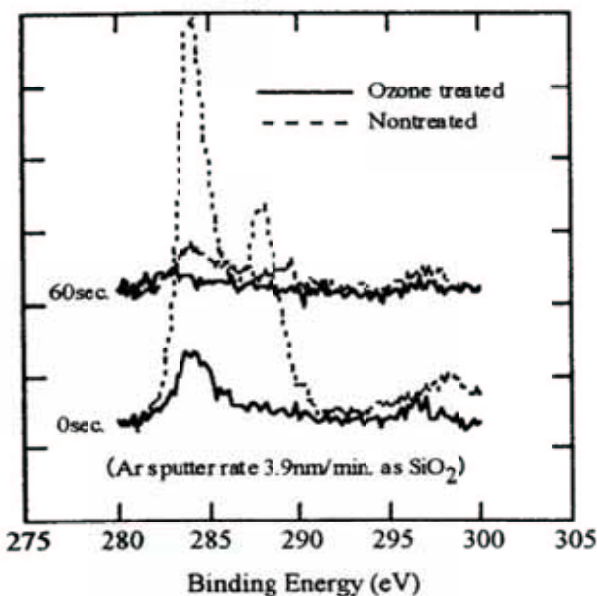


Fig.11 XPS C 1s levels for SS-304 after sputtering of 60 sec and no sputtering for ozone treated and no treated.

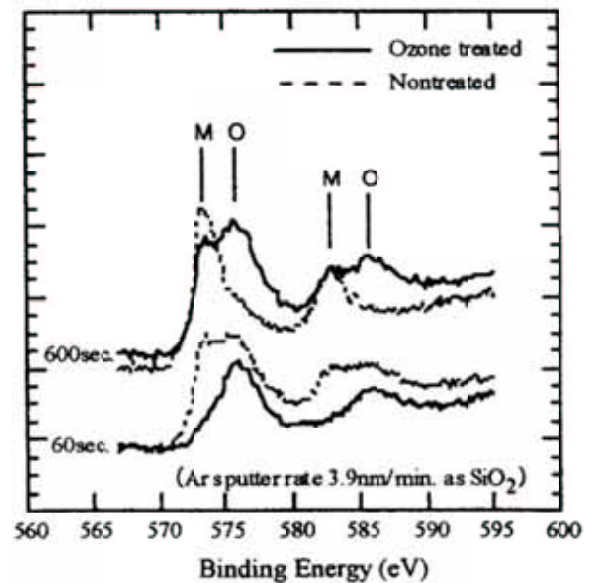


Fig. 12 XPS Cr 2p levels for SS-304 after sputtering of 60 sec and 600 sec for ozone treated and no treated. (M-Metallic chromium, O-Chromiumoxide)

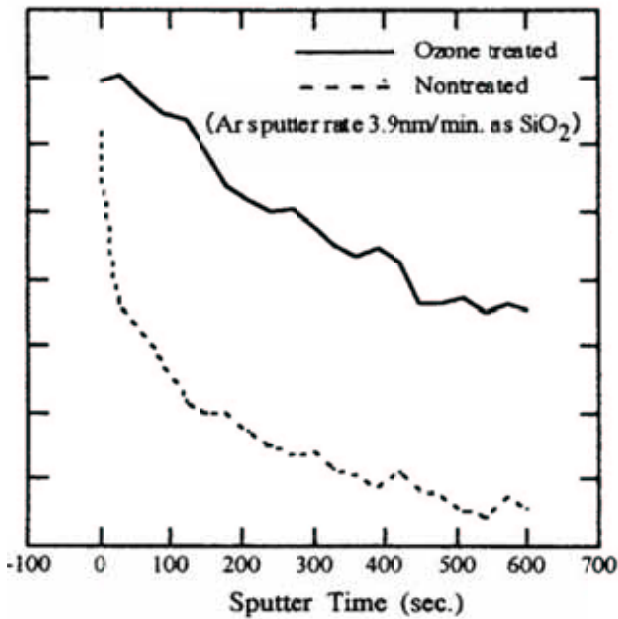


Fig.13 XPS O 1s sputter profile of SS-304 for an ozonized air and no treated.

Using the specimens contained tritium, the decontamination tests of tritium were performed under the conditions of heating temperature of 400 K, exposure time of 1 hour or 3 hours, ozone gas concentration of 0 ppmv (as a reference) and 400 ppmv, and gas flow rate of 150 ml/min. Ozone gas was produced by ozone gas generator manufactured by Masuda laboratory Inc. In the test, the discharged tritium from specimen was recovered and trapped in water bubbler by flowing air through Hopcalite (as oxidant) heated at 823 K. In order to evaluate the treatment effect and determine the temperature effect of tritium

decontaminated, the reference test was performed in the same condition using the air without ozone.

The specimens before and after treatment were measured by imaging plate autoradiography (ARG; made by Fuji Film Co., model BAS-2000) to evaluate the efficiency of tritium decontamination by comparing the activities of tritium existed on the surface. The contact time of specimen to ARG was for 1 hour, and the detection sensitivity of beta ray of tritium was about 6.7 Bq/PSL (Photo-Stimulated Luminescence). Furthermore, in order to observe the chemical state changes on the surface and in inside of it by the ozone treatment, the analysis using XPS (Photoelectron X-ray spectroscopy; made by Physical Electronic, model PHI-1600) was conducted.

II-3. Result and Discussion

Tritium contained in the specimens was discharged by heating (1073 K) in argon gas flow, and the discharged tritium was converted to water by Hopcalite, then it was trapped in H₂O bubbler. From the analytical result measured by liquid scintillation counter, the total amount of tritium contained in the specimen was average about 1×10^4 Bq, and the absorbed activity of tritium on the surface was about 2,000 Bq each side. It was determined that tritium on the surface was mostly existed as the form of tritiated water.

The experimental results of the ozone gas treatment are shown in Fig. 11-13 and Table-6.

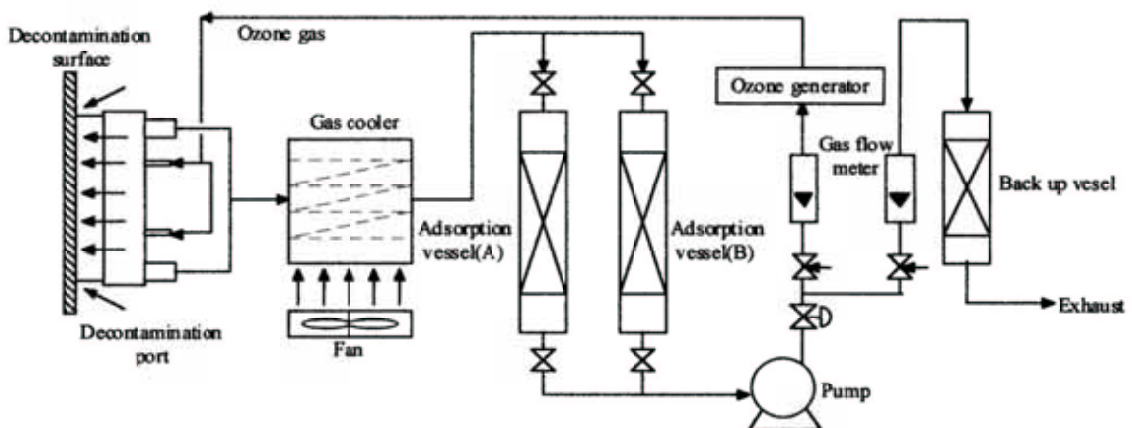


Fig.14 Decontamination system of robot

From the results, the efficiency of tritium decontamination treated with ozone gas was higher than that without ozone, and the higher efficiencies were obtained at the longer treatment. In the cases of stainless steel (NT and EP SS-304), the decontamination efficiencies of over 99 % (less than 5 Bq/cm² of surface contamination density) were obtained for over 1 hour, and the effect of surface conditions of SS-304 was not much

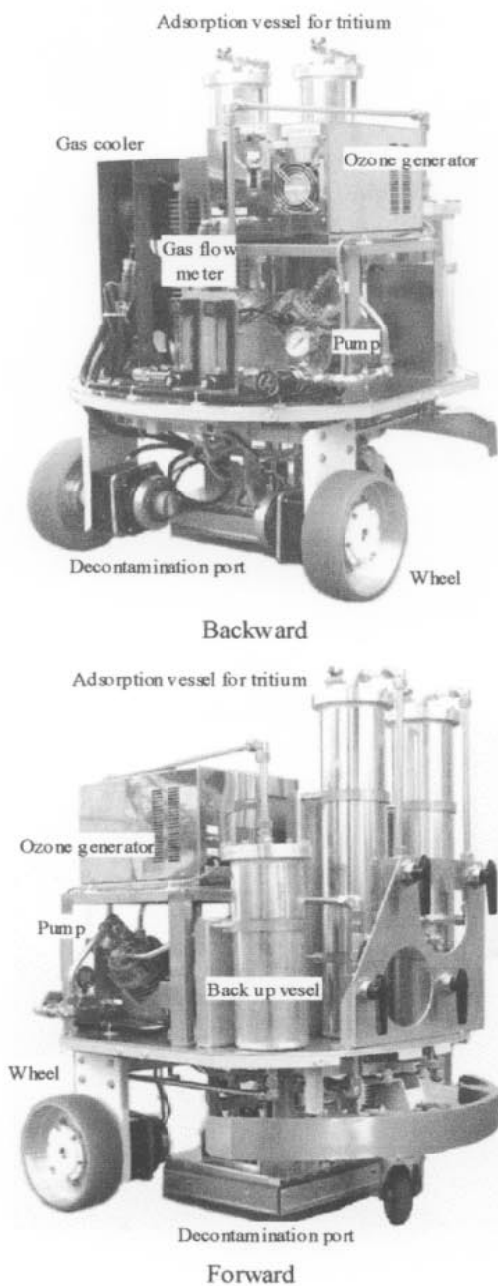


Fig.15 Appearance of completed robot

different. On the other hand, the decontamination efficiencies of aluminum (A-5052) were 80-86 %. By compared the results of SS-304 and A-5052, it was assumed that H₂O and HTO (T: tritium) may be more strongly adsorbed to the hydroxide layer on the aluminum surface than that of stainless steel.

The analytical result using XPS of the carbon atom on the metal surface with and without ozone gas treatment is shown in Fig. 11. From the result, C-1S peak of SS-304 in the case without ozone treatment (dotted line) was very high, but the C-1S peak decreased to about 1/5 with ozone treatment (continuous line). From the result of Ar sputtering treatment (etching rate for 60 seconds: 3.9 nm depth as SiO₂), it was observed that the quantity of the carbon atom in inside of surface layer decreased by ozone treatment, as well. The result indicates that an organic substance combined with tritium may be removed by ozone treatment.

The change of Cr-2P chemical shift by the ozone treatment is shown in Fig.12. After Ar sputtering treatment for 60 s to remove the effect of the organic substance on metal surface, the Cr-2P peaks of both oxide and metal were observed. By the ozone gas treatment, the peak of metal decreased and the peak of oxide became dominant. The oxide peak of Cr-2P after Ar etching for 600 s increased largely. The result was proven that the oxidation was proceeded in inside, and it was also confirmed from the sputter profile of the oxygen shown in Fig. 13. By the ozone treatment, the thickness of oxide layer grew several times, and it is assumed that the adsorbed tritium

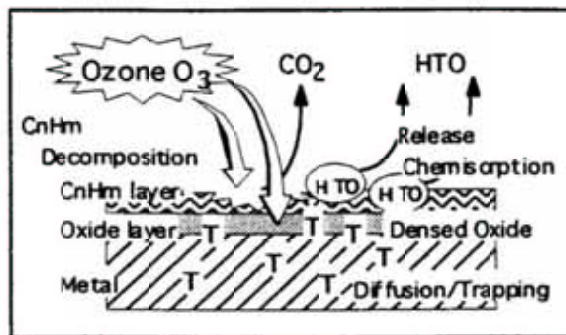


Fig.16 Principle of dry decontamination for tritiated wastes.

was consequentially removed.

II-4. Application: Decontamination Robot for Tritiated Contaminants³⁾

For a routine cleaning and a primary decontamination of decommissioning, a decontamination robot based on dry method of ozone gas treatment was developed for tritiated contaminants. The robot sized of 720(W)x850(D)x1,050(H) mm with a remote and automatic system consists mainly of a flat decontamination vessel of about 1,000 cm² for ozone exposure with a heater and surrounding rubber curtain for preventing suction of outer air, ozone gas generator of surface discharge type made by Masuda Institute Co., a cooling vessel for hot air with ozone, a moisture trap packed molecular-sieves for dryer, and circulation pump. The characteristic of the robot is non-exhaustion type for preventing tritium scatter, and a hot air (120 °C) of 20-30 L/min with ozone about 400 ppmv controlled is continuously circulated in the system of the robot with trapping tritium decontaminated. The decontamination system and the appearance of robot with self-driving loaded battery are shown in Fig. 14 and Fig. 15.

The robot is suitable for using as a routine cleaning and a primary decontamination of decommissioning. In the future, the robot must be advanced to be useful in a practical site.

II-5. Conclusion

With regard to tritiated contaminants, a newly developed concept and technology of gas-phase decontamination, which is an advanced waste-management technology, were proposed.

This study obtained the following results;

1. By the treatment of exposure ozone gas of 400 ppmv at 400 K, in the cases of stainless steel, the decontamination efficiencies of over 99 % were obtained for over 1 hour.
2. By the treatment in the same condition, the decontamination efficiencies of aluminum were

80-86 %.

3. By the treatment of ozone gas, the quantity of the carbon atom on the surface and in inside layer were decreased, and the oxidation on surface and in inside was proceeded.

An assumed principle of the tritium decontamination by the ozone gas treatment is shown in Fig. 16. It is considered that the tritium exists in 3 places that (1) in the organic substance adsorbed on metal surface, (2) the metal atom (not oxide) existed on the surface by chemical adsorption, (3) the metal phase in inside by diffusion. By the ozone gas treatment, it may be assumed and expected that (a) the oxidation of organic substance on the surface combined tritium is proceeded and tritium is easily released as a form of water, and (b) the recombination, release and diffusion to the surface of tritium are prevented by a rigid oxide layer generated.

The ozone gas treatment is easy to use and apply in practice with a simple and safe operation. Furthermore, gas-phase decontamination technology has many advantages over conventional wet methods, in particular, its simple control processes and small secondary waste. The proposed decontamination technology has the sufficient ability and potential to simplify a decontamination operation and reduce the large volumes waste.

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