

PRACTICAL GASEOUS CO-DECONTAMINATION FOR CP, FP AND TRU BASED ON CHEMICAL PLASMA REACTIONS

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ABSTRACT

The treatment conditions and apparatus system of the practical gaseous co-decontamination utilizing chemically reactive plasma treatment were found out. Utilizing chemically reactive plasma, we have developed the simultaneous decontamination technology for the major troublesome nuclides of Corrosion Products (CP; ^{58}Co , ^{60}Co , ^{63}Ni , etc.), Fission Products (FP; ^{99}Tc , ^{106}Ru , etc.) and Transuranium (TRU; U, Pu, Np). Active carbonyl and fluorine generated by discharging CF_4 , CF_4+O_2 , $\text{C}_2\text{F}_6+\text{O}_2$, SF_6 , NF_3 , etc. have the decontamination performance by converting heavy metals radioactive nuclides to gaseous compounds as carbonyl and fluoric compounds. The decontamination data of high removal efficiency were in the both cases by the chemically reactive plasma treatment using DC ($\sim 1,000$ V) and RF (13.56 MHz) discharges. ^{60}Co and U on stainless steel were removed 97 % and above 99 %, respectively, as gaseous forms by one-time plasma treatment with CF_4+O_2 gas pressure of 0.4~1.6 Torr and a flow rate of 25~50 ml/min for 2~15 min at room temperature. On the other hand, the volatility of ^{137}Cs was not observed or very small (0~13 %) as presumption.

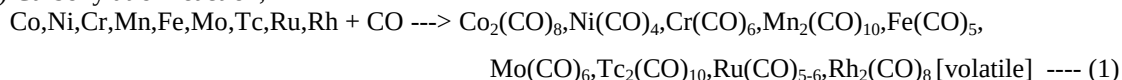
Further, to apply the chemically reactive plasma treatment as a practical decontamination method on an actual large equipments of nuclear sites, three types of plasma of Electron Cyclotron Resonance (ECR) at about 1 mTorr, Down-Stream Micro Wave at less than 100 Torr and Corona Discharge at about atmospheric pressure are being tested and compared, and a trapping method of volatile nuclides also are under investigation.

INTRODUCTION

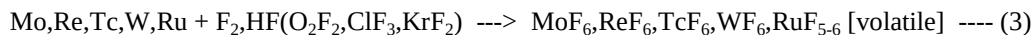
Decontamination and volume reduction of the radioactive wastes generated by atomic power plants, nuclear fuel reprocessing plants and nuclear research institutes has proven to be extremely difficult. In regard to a material's surface contaminated by actinides (ie. U, Pu), gas-phase decontamination technology using fluoric gases (dioxygen-difluoride O_2F_2 , chlorine-trifluoride ClF_3 , krypton-difluoride KrF_2) to convert them to fluoric compounds (hexafluoride forms) has been already proposed and developed [1-10, 15], and the fluoric plasma treatment using NF_3 gas for decontamination of U was reported recently [14]. However, the gas-phase decontamination technology for radioactive transition elements and the technology to decontaminate both radioactive transition elements and actinides (co-decontamination of corrosion products: CP, fission products: FP, trans-uranium: TRU) on a surface have never been studied or proposed.

We have developed a new gas-phase decontamination technology based on gaseous reactions utilizing volatile properties of carbonyl compounds and fluoric compounds of CP, FP and TRU on a material's surface [11-13]. Carbonyl compounds of normal transition elements including CP and FP have volatile properties, and some fluoric compounds of FP and TRU also have volatile properties. Because the carbonyl and fluoric compounds have thermal properties giving them low melting points, low boiling points, and/or low sublimation points, many of these compounds can become gaseous or volatile at a lower temperature, such as room temperature. The developed decontamination method based on carbonyl and fluoric gaseous reactions is a new concept as a decontamination technology for nuclear wastes. We have determined the feasibility of new gaseous decontamination technology by four treatment methods; (1) by the treatment under a high CO pressure (50~200 atm) and a high temperature (about 350 °C), (2) by the pretreatment supercritical CO₂+I₂+H₂O and the subsequent gaseous reaction, (3) by the plasma treatment using F₂ gas or a non-toxic gas mixture (ab. 1 Torr) of CF₄ and O₂ under the safe and mild conditions such as reduced pressure, shorter time periods, and ambient temperature, and (4) by the fluoric chemical reaction using ClF₃ gas to remove TRU deposits by converting them to gaseous fluoric compounds (eg. UF₆) at room temperature and without the use of plasma treatment. From the results, it has been verified that the chemical reactions involving carbonylation and fluorination reactions can be utilized for gas-phase decontamination, and the potential for this new idea for decontamination has been affirmed. The related chemical reactions utilized are indicated by Eqs. (1)-(3) [11-13];

(a) Carbonylation reaction;



(b) Fluorination reaction;

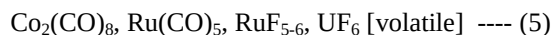
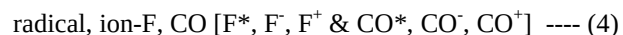
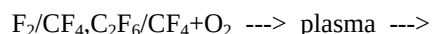


The gaseous co-decontamination of many troublesome nuclides of CP, FP and TRU may be possible when both carbonylation and fluorination reactions occur at the same time.

In four methods mentioned above, it is affirmed that the chemically reactive plasma treatment and the chemically reactive gas treatment are practical; in particular, the plasma treatment may be useful as a co-decontamination treatment of CP, FP and TRU. The purpose of this study is to compare the several types of plasma treatments as the practical gas-phase co-decontamination method.

Plasma Treatment for Co-Decontamination

To decontaminate under a safe and mild conditions, the treatment is carried out using plasma under the conditions of room temperature and reduced pressure to generate the unstable and highly reactive carbonyl and fluoric species. 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) [12, 13];



The concept of the chemically reactive plasma treatment is shown in Fig. 1.

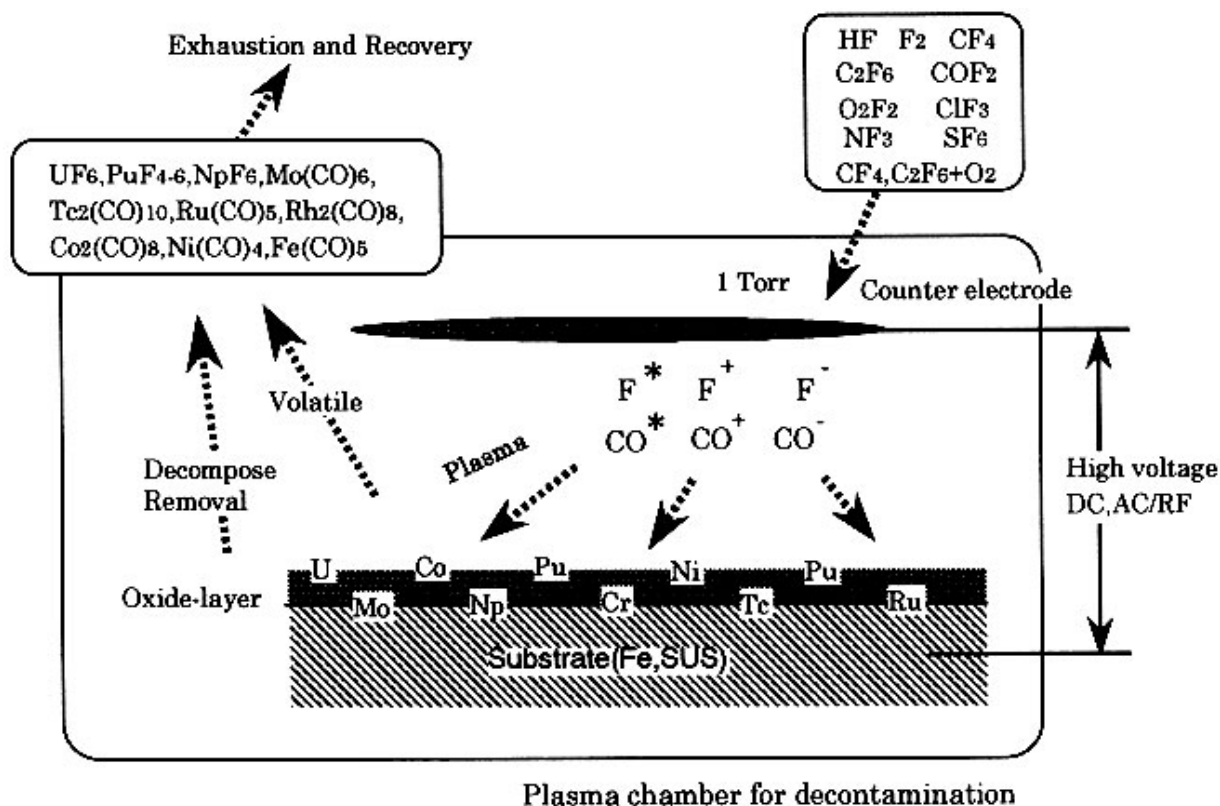


Fig. 1 (Concept of chemically reactive plasma treatment)

EXPERIMENT

The experimental apparatus consisted of gas cylinders containing Ar, O₂, F₂, CF₄, NF₃ and SF₆, a plasma reaction chamber (maximum od. 254 mm, approximate volume of 10 L; speciflicated vacuum chamber made of stainless steel SUS304) with many flanges for introducing plasma gas, vacuum gauges, manipulators for introducing contaminated test samples, viewing windows onto the chambers, two Baratron system (made by MKS Co.; detectable ranges are maximum 1000 and 1 Torr with the measurable range ratio of 10⁵) to measure the reduced pressure after introducing gases, a quadrupole mass spectrometer (QMS) for measuring plasma and residual gases, a halogen gas trap (Halogen-filter: made by Nippon Sanso Co.; type SS-21) positioned in front of the vacuum pump, and a halogen monitor to detect potential gas leaks and to monitor the performance of the halogen trap. Furthermore, the power suppls for dischrages of DC and RF (or ECR, Down-Stream Micro Wave and Corona) to produce plasma are assembled.

To evaluate the decontamination efficiency of various nuclides by plasma reaction, two kinds of radiation detectors for measuring alpha- and gamma-rays were used to monitor the removal efficiency of nuclides from the contaminated material. Initially, the test samples (SUS304: round-plate) with mounting predetermined amounts of radioactive nuclides of ^{60}Co , ^{137}Cs , and U diluted by nitric acid solution (0.01~0.1 mole/L) were heated in an oven to dry at about 110-120 °C. Some of the test samples of stainless steel were heated for 1 h at 500 °C in air in an electric furnace. By this pretreatment, a reddish-golden oxide layer grew on the surface of stainless steel, which contained radioactive nuclides. After placing this pretreated sample onto the sample holder inside plasma chamber, remaining air in the reactor was completely evacuated. Next, the plasma was generated into the chamber by introducing the plasma reaction gases. Tests were performed varying the pressure of reaction gases, treatment time, the kinds of gases, the pretreatment conditions of contaminated samples, and the type of nuclides (^{60}Co , ^{137}Cs , and U).

Experimental conditions were set up as follows;

1. Plasma gases : F_2 , CF_4 , C_2F_6 , NF_3 , SF_6 , CO_2 , CH_4 , O_2 , H_2
(high purity, packed in metal cylinder)
2. Condition of gases : contained in the chamber or flowing (25~75 cc/min.)
3. Treatment time (Discharged time) : 2~15 min.
4. Plasma sources : DC (540~1020 V), RF (13.56 MHz)
5. Gas pressure : 0.3~1.6 Torr
6. Mounting materials of nuclides : stainless steel[SUS304]
round-plate of diameter 1 inch
7. Nuclides : ^{60}Co , ^{137}Cs , U (UO_2^{2+}) as nitrate
8. Treatment temperature : room temperature

RESULTS AND DISCUSSIONS

a) By DC Plasma;

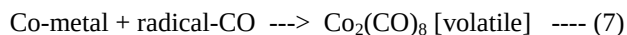
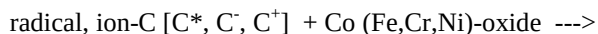
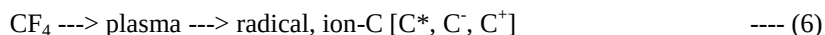
To determine the feasibility of the plasma treatment as a gas-phase decontamination technology, a fundamental test of DC plasma was performed. The results of the feasibility tests are outlined below. For greater detail of these treatments, see Refs. 12 and 13.

U was removed by plasma treatment using F_2 gas. The removal efficiency of U was sensitive to F_2 pressure (0.3~1.4 Torr), and also depended on the discharged voltage (540~1,020 V). The effect of the treatment time (discharged time) was not so large for any period exceeding 2 min. U was decontaminated with a high efficiency for a short time, and the fluorination utilized DC plasma treatment is feasible in decontaminating TRU and some FP.

Next, using non-toxic gases, co-decontamination 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. The result on co-decontamination of Co-60 (12.5 kBq) and U (2.1 Bq) is that the removal efficiency of U 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 TRU). The result of the mixed gas plasma of CF₄ and O₂ to remove the thick U layer (approximate 10 μm thick of U₃O₈) on stainless steel shows that the thick U layer was completely removed by the treatment of chemically reactive plasma. The gaseous U-fluoride and excess unreacted fluorine gas were completely trapped by the Halogen-filter. We conclude, 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 carbonyl and fluoric species. Tests using cobalt-60 and U were conducted to examine the pretreatment effect of H₂ gas for reduction of the chemical forms of target nuclides, thereby reducing the valency of the U-compound. Judging from the removal data of cobalt-60, it can be said that 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 oxidized metal surface. As the most likely reason, cobalt-60 pretreated by oxidization 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. (6)-(7) indicate the presumptive behavior. The effects of the H₂ pretreatment, on the other hand, was not as obvious.



b) By RF Plasma;

To compare RF plasma with DC plasma, the co-decontamination efficiency of mixed contamination of ⁶⁰Co (400 Bq), ¹³⁷Cs (40 Bq) and U (0.1 mg) was evaluated. In the tests, the utilization of magnet for gathering the plasma gas to the target test sample was performed, too. The experimental result is shown in Table I. The result shows that the decontamination efficiencies by plasma treatment of DC, RF and RF with magnets are not so much different, and CF₄+O₂ gas may be suitable as the plasma gas for co-decontamination. It is presumed that a bit volatility of ¹³⁷Cs was caused by heating of sample holder or electrode by the discharge.

Table I Comparison of DC, RF and RF with magnets

^{60}Co (400 Bq), ^{137}Cs (40 Bq) and U (100 μg) on SUS304 plate (1 inch), gas flow: 25~50 ml/min., discharging time: 15 min., gas pressure: 0.9~1.6 Torr, DC voltage: 600~1,200 V, RF power: 100~300 W (13.56 MHz).

plasma gas	kind of plasma	Removal rate ^{60}Co	removal rate ^{137}Cs	removal rate U
CF_4+O_2 (12 %)	DC	70~97 %	0~13 %	86~94 %
	RF	88~97 %	0~ 6 %	92~99 %
	RF+magnets	89~95 %	0~ 8 %	89~99 %
$\text{C}_2\text{F}_6+\text{O}_2$ (12 %)	DC	23~25 %	4~12 %	47~48 %
	RF	~ 0 %	0~ 6 %	9~13 %
NF_3	DC	67~71 %	0~ 5 %	> 99 %
	RF	0~ 1 %	0~ 3 %	80~90 %
	RF+magnets	0~ 2 %	0~ 7 %	80~90 %
SF_6	DC	48~50 %	0~ 1 %	89~96 %
	RF	~ 0 %	~ 0 %	0~ 6 %

Next, the positions of test samples in the RF plasma were investigated. The conditions of RF plasma and test samples were similar as mentioned above. The result (Table-II) shows that the positions of test samples in RF plasma were not so much different. In the cases of the treatment of inside pipe and that with a slit and a hole, the results with high removal efficiency are particularly interesting.

Table II Effects of sample position by RF plasma

^{60}Co (400 Bq), ^{137}Cs (40 Bq) and U (100 μg) on SUS304 plate (1 inch), gas flow: 25~50 ml/min., discharging time: 15 min., gas pressure: 0.9~1.6 Torr, DC voltage: 600~1,200 V, RF power: 100~300 W (13.56 MHz).

plasma gas	sample position	removal rate ^{60}Co	removal rate ^{137}Cs	removal rate U
CF_4+O_2 (12 %)	2 cm from plasma (surface *1)	97 %	5 %	98 %
	2 cm from plasma (back *2)	94 %	5 %	97 %
	8 cm from plasma (surface)	93 %	3 %	95 %
	edge inner pipe (id. 1 inch)	35 %	8 %	82 %
	10 cm inner pipe (id. 1 inch)	24 %	2 %	59 %
	in pipe with 0.1mm slit	36 %	5 %	83 %
	in pipe with 1 mm $\varnothing$ hole	69 %	3 %	90 %
NF_3	2 cm from plasma (surface)	1.5 %	8 %	93 %
	8 cm from plasma (surface)	0 %	3 %	90 %

*1 : "surface" means that the face contaminated by radioactive nuclides looks plasma gas flow.

*2 : "back" means that the face contaminated by radioactive nuclides looks opposit to plasma gas flow.

Furthermore, at present, to apply the chemically reactive plasma treatment as a practical decontamination method on an actual large equipments of nuclear sites, three types of plasma of Electron Cyclotron Resonance (ECR) at about 1 mTorr, Down-Stream Micro Wave at less than 100 Torr and Corona Discharge at about atomospheric pressure are being tested and compared, and a trapping method of volatile nuclides are also under investigation.

Applications

If gas-phase decontamination technology will be practicable, it may be available and economically advantageous because of the difficulties to decontaminate and treat the large volume of nuclear wastes; especially non-incinerable radioactive wastes. Compared to the current decontamination methods of wet-chemical, physical, and mechanical treatments, gas-phase decontamination has many superior characteristics, of which the primary advantages are the easy handling and simple controlling processes, small secondary waste (by-products), and most importantly the ability to use even small-sized equipment for in situ decontamination.

It is important to use the proper treatments and techniques particular to the contaminated material or device, whenever decontaminating radioactive wastes. A practical model of the equipment developed for the gas-phase decontamination is shown in Fig. 2. The model utilizes Electro Cyclotron Resonance (ECR) plasma to generate radical carbonyl and fluoric chemical-species is practicable for the gas-phase decontamination, since it has the specific ability to induce the reactive carbonyl and fluoric species into an isolated reaction chambers.

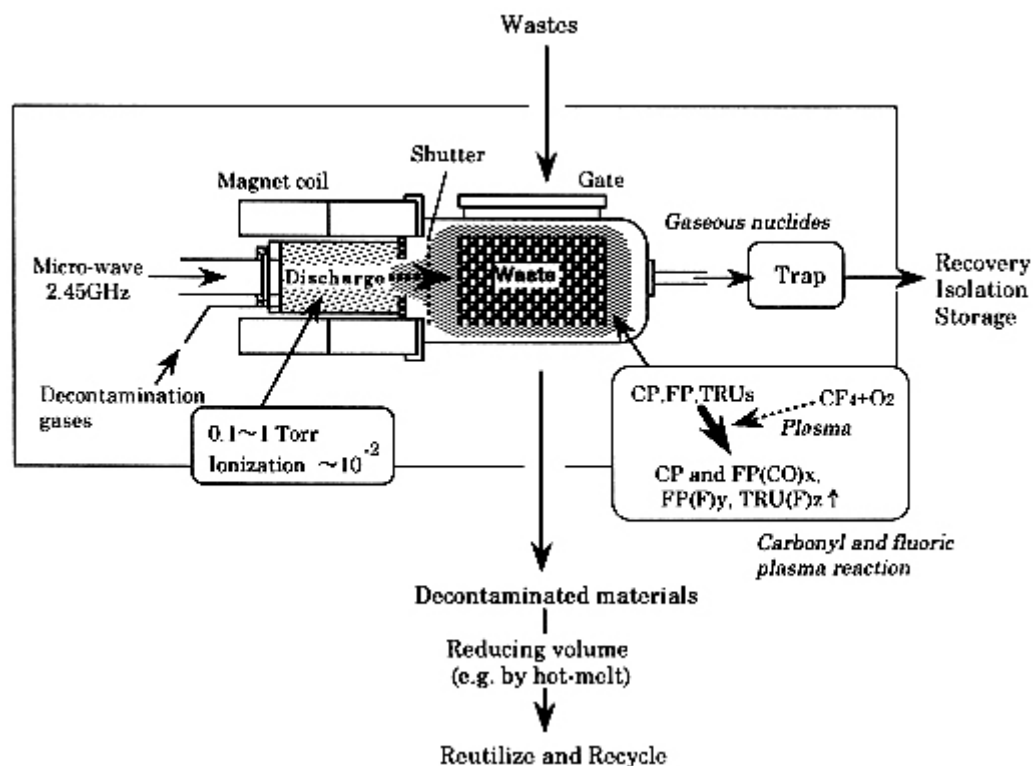


Fig. 2. Practical equipment for plasma decontamination

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 wastes created each year or non-incinerable radioactive wastes, which

include burned-ash, many kinds of used-metals, and discarded equipment.

CONCLUSION

In regard to a surface contamination, the chemically reactive plasma treatments as a new conceptual gas-phase decontamination, which is an advanced practical waste management technology, were tested.

The results obtained in this study are summarized below;

(1) By the treatment of DC plasma;

Using radical fluoric species by DC plasma treatment of F_2 gas, U was decontaminated with high efficiency. In the case of generating carbonyl and fluoric species using non-toxic gas mixture (CF_4+O_2), we verified that U and ^{60}Co were removed simultaneously with the high removal efficiency.

(2) By the treatment of RF plasma;

From the results of RF plasma compared with DC plasma, the decontamination efficiencies of ^{60}Co , ^{137}Cs and U by plasma treatment of DC, RF and RF with magnets are not so much different. And, CF_4+O_2 may be suitable for co-decontamination as the plasma gas. In the RF plasma, the positions of sample were not so much affected. The decontamination feasibility of inside pipe and that with a slit and a hole was found out.

From the experimental results, the chemically reactive plasma treatment of carbonylation and fluorination has a ability to decontaminate of mixed contamination of CP, FP and TRU, simultaneously.

One drawback of the newly-developed technology is that it does not encompass the decontamination and removal of alkali metals elements (e.g. cesium) and alkali earth metals elements (e.g. strontium, barium), because of their different chemical properties as well as the underlying basis for the decontamination principle. Though we have yet to examine conditions which would allow for the inclusion of alkali metals and alkali earth metals in the technology including rare earth elements, such research is due to take place in the near future.

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