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EXPERIENCE OF TEST OPERATION FOR REMOVAL OF FISSION PRODUCT NUCLIDES IN TRU-LIQUID WASTE AND CONCENTRATED NITRIC ACID USING INORGANIC ION EXCHANGERS

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ABSTRACT

From 1968 to 1969, about 200g of highly purified plutonium were recovered from the spent fuel (aluminum clad, metal Uranium, 600MW/T) of JRR-3 research reactor by the reprocessing research plant (Purex) of JAERI's Reprocessing Test Facility (JRTF).

Various radioactive liquid wastes including TRU (a total volume of 70m3) were generated during reprocessing. These liquid wastes were kept in storage tanks and JRTF was studying new technical means of removing radioactivity from them.

Of these wastes, the FP liquid waste still has relatively high level beta and gamma radioactivity, TRU nuclides (Pu: 2.7×10^3 Bq/ml, beta: 5.6×10^6 Bq/ml, gamma: 1.8×10^6 Bq/ml) and concentrated nitric acid, because it was discharged from the co-decontamination process.

During fiscal 1995 and 1996, a new treatment system was constructed and installed in the existing building built to store the above mentioned liquid wastes. The system includes two processes to remove plutonium, cesium and strontium. Fibrous activated carbon (FAC) adsorbent, developed by JAERI and Unitika Ltd. was used to remove plutonium, and inorganic ion exchangers developed and manufactured in Finland by IVO (presently Selion Oy) were used to remove cesium and strontium. The whole system, including remote handling system and attached subsystems was implemented for JRTF by Mitsui Engineering & Shipbuilding Co..

The pH of the liquid waste after passing through Pu removal column, filled with FAC, was adjusted for best performance in the Cs/Sr removal column. In order to remove cesium and strontium from waste solution, the controlled liquid waste was sent to Cs/Sr removal column, which was filled with a mixture of hexacyanoferrates and titanium oxides. The system's treatment capacity is 55 litters per batch. The equipment's, such as the removal columns, tanks, pumps, and handling devices for column exchange, treated waste sampling, etc. are accommodated in a small steel shielding cell about 2 meter wide, 3 meter long and 3 meter high.

A plutonium decontamination factor (DF) of more than 10 was achieved with FAC in the range of 1-0.5 M nitric acid, and plutonium adsorption was 0.31mg Pu/g FAC. High selectivity was also confirmed by the coexistence of nuclides in the waste such as cesium and strontium, which were not adsorbed.

A high cesium and strontium DF of more than 10^3 was achieved through the use of hexacyanoferrates and titanium oxides in the pH range of 9-10.

From these results, radioactive removal process using inorganic ion exchangers was also demonstrated in an engineering scale plant.

INTRODUCTION

The amount of radioactive waste including TRU generated by the reprocessing and MOX fuel plants is expected to increase with the expansion of nuclear fuel cycle industries.

On top of that those wastes vary in from and sort, so it is very important to verify that they can be treated safely. JRTF has stored the liquid wastes generated by JAERI's reprocessing research plant, and developed efficient treatment technologies to remove TRU from such wastes.

Recently, the treatment of FP Liquid Waste containing TRU and relatively high level beta and gamma radioactivity generated by the co-decontamination process of the reprocessing research plant, has been carried out with a new treatment system using inorganic adsorbents.

The main nuclides included in the waste are plutonium, strontium and cesium. The operational experience with this treatment system is reported in detail in the following.

This report constitutes some of the results obtained through a study financed by the Science and Technology Agency (STA) of Japan.

OUTLINE OF THE TREATMENT SYSTE

Properties of the FP Liquid Waste

The FP Liquid Waste was generated by the co-decontamination process of the reprocessing research plant, which was the first engineering scale plant in Japan. It contains TRU and relatively high level beta and gamma radioactivity and concentrated nitric acid. Table 1 shows properties of the FP liquid waste.

Table.1 Property of Fission Product Liquid Waste

Pu concentration	Bq/ml	2.7×10^{3}
	mg/ml	1.2×10^{-3}
U concentration	Bq/ml	4.7×10^{1}
	mg/ml	1.6×10^{0}
Gamma (Cs-137) Radioactivity	Bq/ml	1.8×10^{6}
Gross beta Radioactivity	Bq/ml	5.6×10^{6}
Dissolved metal Na	mg/ml	8.4×10^{-1}
Al		3.7×10^{-2}
Fe		2.1×10^{-1}
Cr		2.9×10^{-2}
Ni		1.7×10^{-2}
Zr		2.0×10^{-2}
Acidit	M	1.7

Outline of the Treatment System

Figure 1 shows a flow diagram of the treatment system.

The system is installed in the existing building built to store the above mentioned liquid wastes, and most of the equipment including remote handling devices is installed in a small steel shielding cell. The cell size is approximately 2 meter wide, 3 meter long and 3 meter high, with 200 mm thick wall.

The equipment can treat 55 litters per batch, which is capacity of the liquid waste receiver tank inside the cell. For the first, the liquid waste is siphoned from storage tank, which is located in an underground concrete cell, into the receiver tank using an air jet inside the cell. The liquid waste then flows successively through the Pu removal column, the pH adjusting tank, the filter column, and the Cs/Sr removal column.

The waste is then pumped into the top of the Pu removal column, filled with Fibrous Activated Carbon (FAC), and flows out under gravity from the bottom into pH adjusting tanks.

The pH of the waste is adjusted in the pH adjusting tank to optimize the performance of cesium and strontium removal. The adjusting reagents are a 10 M NaOH solution for rough adjustment and a 1 M NaOH solution for fine adjustment. The pH of the adjusted waste is from 9 to 10.

After the adjustment, the waste is sent to Filter column and the following Cs/Sr removal column with a pump. Precipitation sludge generated by pH adjustment is separated from solution by a ceramic filter (1 micron pore size) in Filter column. The filtrated solution then flows into the Cs/Sr removal column, filled with both hexacyanoferrates to remove Cs in the lower part and titanium oxides to remove Sr in the upper part.

Finally, treated waste is stored in a treated waste tank where it is sampled and measured its radioactivity, and then, it is confirmed that the radioactivity satisfies the JWTF (JAERI's waste treatment facility) acceptance criteria (Alpha: $<3.7\times10^{2}$ Bq/ml, beta and gamma: $<3.7\times10^{4}$ Bq/ml, alpha/beta and gamma: <0.1). After that, treated waste is transferred to the JWTF.

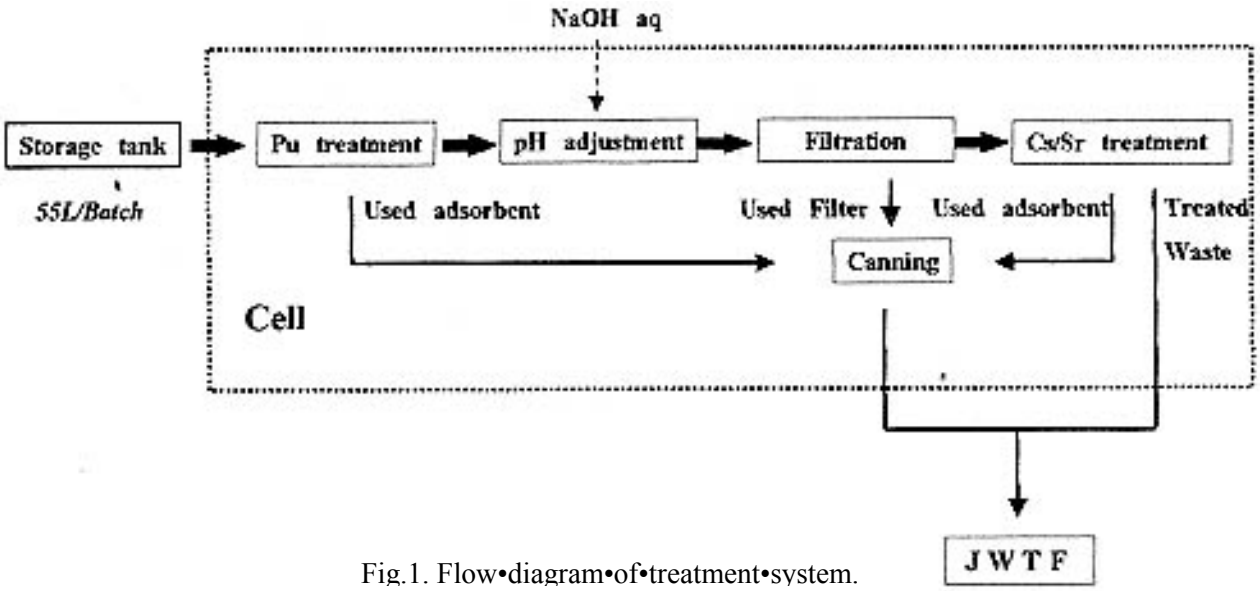

Fig.1. Flow•diagram•of•treatment•system.

The residual water in the used column is sucked up by an air jet. The used column is put into a lead shielded 200-litter drum, and transferred to the JWTF.

Basic Conditions

The basic conditions of Pu removal column and Cs/Sr removal column are set out below;

1) Fibrous activated carbon adsorbent (for Pu removal)

-Constitution	: high hydrophilic fibrous activated carbon (80 %)
	: Inorganic binder (20 %)
-Form	: 155mm diameter x 465mmH (93mm x 5 layers)
-Weight	: about 2000g
-Volume	: 8.8 liter
-Flow direction	: downwards
-Flow rate	: 15 liters/hr
-Space velocity	: 1.65 h^{-1}

2) Hexacyanoferrates and titanium oxides (for Cs/Sr removal)

-For cesium removal	: hexacyanoferrates (in lower part)
-For strontium removal	: titanium oxides (in upper part)
-Volume	: about 0.82 liter each
-Grain size	: 0.3 to 0.85 mm
-Flow direction	: upwards
-Flow rate	: 15 liters/hr
-Space velocity	: 18 h^{-1}

OPERATIONAL TEST OF Pu AND Cs/Sr REMOVAL USING INORGANIC ADSORBENTS TEST ITEMS

Estimation of Plutonium Removal Performance

The following tests were carried out to estimate what parameters affect plutonium adsorption performance.

Space velocity

In order to estimate the effect of space velocity (SV), two cases test at SV of 1.65 h^{-1} and 0.90 h^{-1} were carried out.

Concentration of nitric acid

It was found that the dipping test of FAC demonstrated a good performance in 1 M solution and it deteriorated slowly with increase in acid concentration. Accordingly, in order to confirm the effect of acid concentration, the acid concentration of the original waste was reduced from 1.7 M to around 1-0.5 M.

Estimation of the Performance of Cesium and Strontium Removal

It is said (ref.1) that hexacyanoferrates used for cesium removal are less dependent on pH and that titanium oxides used for strontium removal demonstrate best performance at a pH higher than 9 (ref.2). To confirm the effect of pH, three test were carried out at pH5-8, pH9-10, and pH11-12

The Experiment

To study adsorbent characteristics, radioactivity breakthrough curves are plotted with the radioactivity concentration ratio (C/Co) and ratio of treated volume to adsorbent bed volume (BV).
The radioactivity concentration ratio, and radioactivity quantity are calculated with the following equations.

-Radioactivity concentration ratio [-]	= C / Co
-Decontamination factor (DF)	= Co / C

-Reduction ratio [%] = [(Co – C) / Co] x 100
-Adsorbed radioactivity quantity [Bq or mg] = (Co x Vo) – (C x V)
Co: radioactivity concentration before treatment [Bq/ml]
C : radioactivity concentration after treatment [Bq/ml]
Vo: liquid waste volume before treatment [ml]
V : liquid waste volume after treatment [ml]

Alpha and gamma radioactivity analyzers employing silicon and Ge semiconductor detectors were used, and overall beta activity was analyzed using 2π gas flow counter.

RESULTS AND DISCUSSION

Estimation of Plutonium Removal Performance

Figure 2 shows the plutonium breakthrough curve. In this graph, the ratio of treated volume to absorbent bed volume (BV) is on the horizontal axis, and the plutonium concentration ratio of in to out streams is on vertical axis.

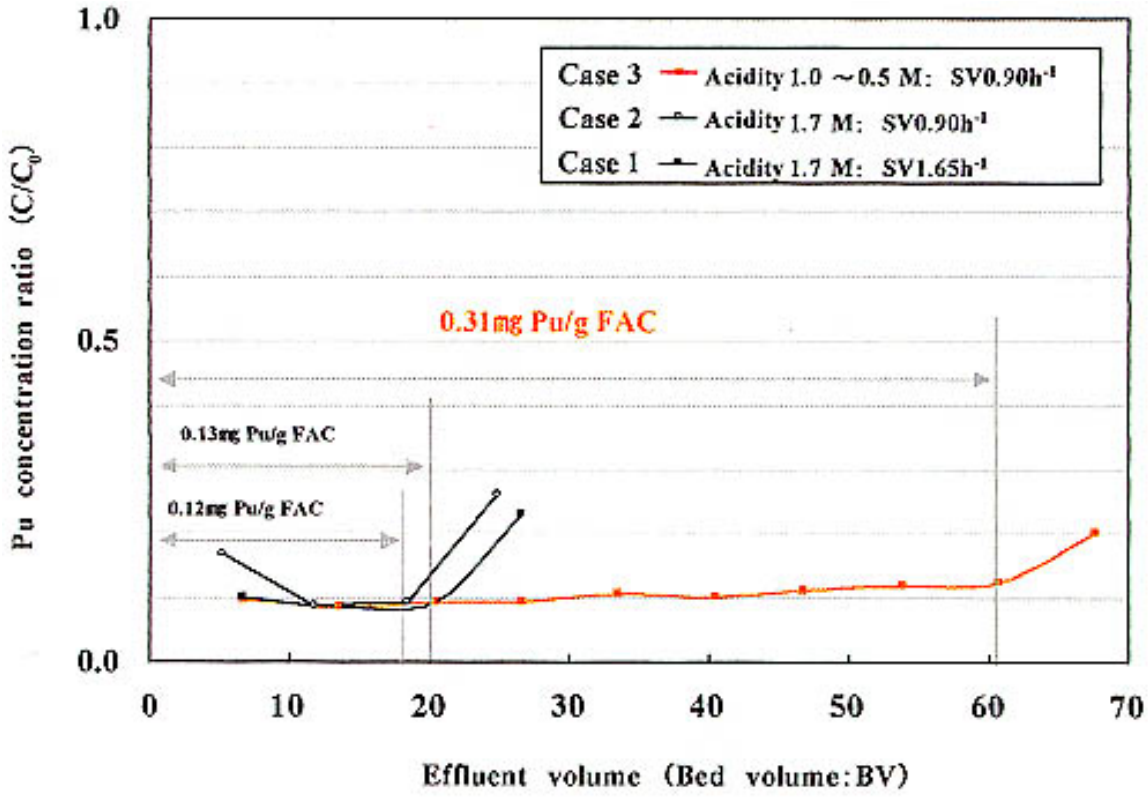

Fig.2. Breakthrough•curve•of•Pu.

Effect of space velocity (SV)

Test case 1 was carried out with 1.65 h^{-1} SV. In this case, the plutonium concentration ratio of in to out streams in the initial term showed 0.1, but it increased markedly after around 20 BV. The quantity of adsorbed plutonium was 0.13mg Pu/g FAC at that time, which was worse than the design value. To increase average contact time of waste with adsorbent than that in case 1, test case 2 was carried out with 0.90 h^{-1} SV. However, Difference of performance between case 1 and case 2 was not confirmed. Therefore, space velocity from 1.65 to 0.9 doesn't affect Pu removal performance.

Effect of nitric acid concentration

In test case 3, waste acid concentration was kept at 1-0.5 M by adding a 10 M NaOH solution. As a result, the plutonium concentration ratio was maintained at 0.1 until more than 60 BV. The resulting adsorbed plutonium was about 0.31mg Pu/g FAC, which is a marked improvement in adsorbent capacity.
From these results, the acid concentration of 1-0.5 M is effective for use of the fibrous adsorbent.

Table 2 also shows other radioactivity concentrations. In this table, beta and gamma radioactivity concentrations did not change before and after passing through adsorbent, confirming that the fibrous adsorbent is highly selective of plutonium in high nitric acid concentration waste.

Table. 2 Results of Pu removing test using the inorganic adsorbent

		Initial solution	Treated solution
Pu concentration	Bq/ml	2.4×10^{3}	2.0×10^{2}
	mg/ml	1.0×10^{-3}	8.6×10^{-5}
U concentration	Bq/ml	4.7×10^{1}	4.1×10^{1}
	mg/ml	1.6×10^{0}	1.5×10^{0}
Gamma (Cs-137) radioactivity	Bq/ml	1.6×10^{6}	1.6×10^{6}
Gross beta radioactivity	Bq/ml	5.2×10^{6}	5.0×10^{6}

Estimation of Cesium Removal Adsorbent Performance

Figure 3 shows cesium adsorption results. Cesium removal design specification call for a waste pH of about 9-10, and that cesium DF to be maintained at more than 400 at 850 BV when treated in the same removal column.

When waste pH was in 5-8 and 11-12, cesium DF was in the 10^3 order in the first period, and was 400 at about 1100 BV treated.

When waste pH was in 9-10, cesium DF was more than 10^3 the first time, and this good performance was maintained at about 1600 BV treated.

These results show that cesium DF was over 10^3 at double the design condition waste volume, demonstrating that hexacyanoferrates are very effective for cesium removal even for relatively high gamma radioactivity concentration waste, and keeping waste pH in the 9-10 is the most effective way to use it.

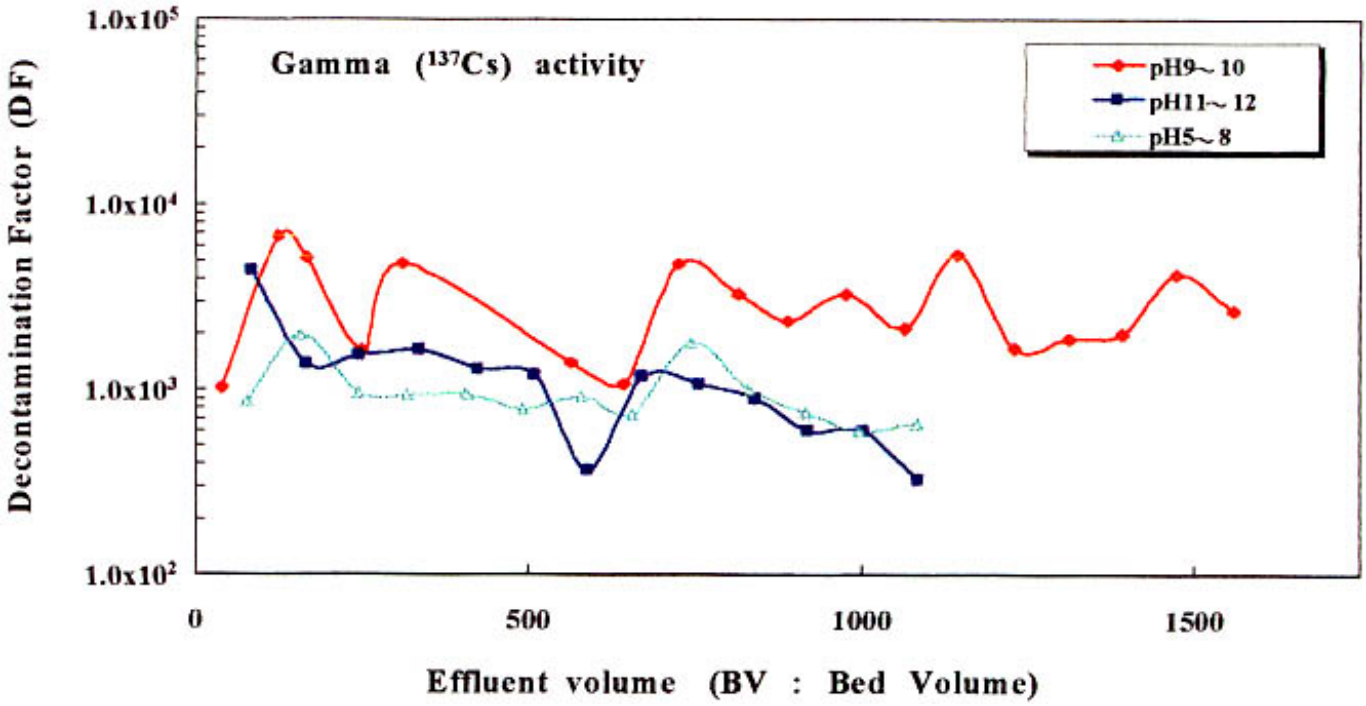

Fig.3. Results•of•Cesium•Adsorption•Treatment•Test

Estimation of Strontium Removal Adsorbent Performance

Figure 4 shows strontium adsorption results. In the design condition for removing strontium, waste pH is to be kept at about 9-10, and strontium DF maintained at more than 200 at 850 BV when treated in the same removal column.

In all cases, waste pH was kept in 5-8, 9-10, and 11-12, and strontium DF was 10^3 in the first period. When waste pH was kept in 5-8 and 11-12, strontium DF was 200 at about 1000 BV treated. When waste pH was in 9-10, strontium DF was 200 at about 1600 BV treated.

These results show that it is possible to treat waste at double the design specifications, titanium oxides are very effective in removing strontium, even for relatively high gamma radioactivity concentration waste, and that keeping waste in the 9-10 pH is the most effective way of removing strontium.

In addition, at that time that test was done with pH 9-10 waste, cesium DF was over 10^3, however, the Cs/Sr removal column had to be changed because the strontium DF was 200 that was the lower limit for use in the same removal column. At that time, beta and gamma radioactivity fixed in the column was 4.2×10^{12} Bq.

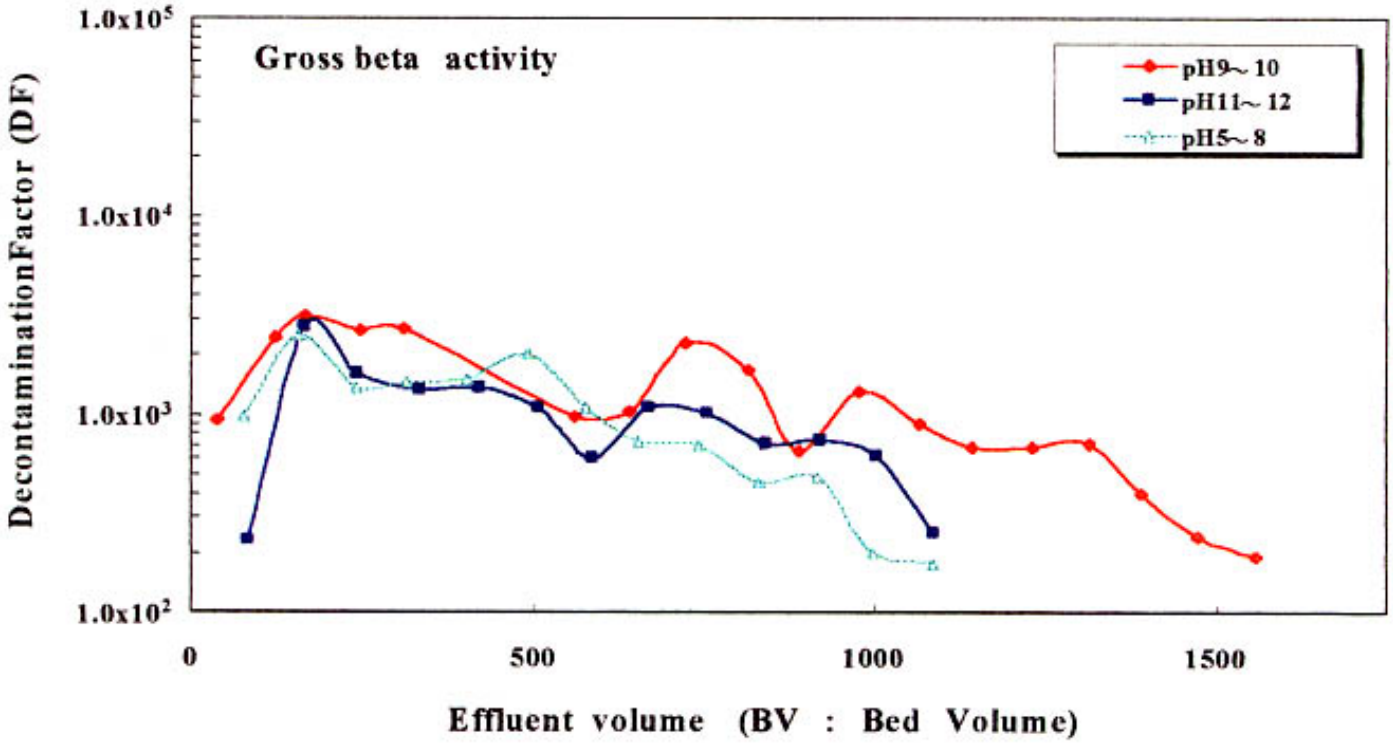

Fig.4.•Results•of•Strontium•Adsorption•Treatment•Test.

CONCLUSION

The following are the results of test operation of the use of an inorganic adsorbent and ion exchangers to adsorb radioactive nuclides from FP liquid waste containing TRU nuclides and high beta and gamma nuclides,.

Tests of the effectiveness of fibrous activated carbon (FAC) for removing Pu,
- FAC is highly selectivity of plutonium.
- There was no SV effect in the 1.65 to 0.90 h^{-1} range.
- Plutonium DF was 10 until 60 BV treatment in the range of 1-0.5 M, and plutonium adsorption capacity was about .31mg Pu/g FAC.

From tests of Cs and Sr removal using the hexacyanoferrates and titanium oxides,
- The DF of beta and gamma radioactivity were indicated to be more than 10^3 ; a very good performance.
- The capacity per column achieved about 1600 BV in the 9-10 pH range,
  And the capacity of beta and gamma radioactivity adsorbent was $4.2x10^{12}$ Bq per column.

Since these tests, an engineering scale plant radioactive removal process using FAC and inorganic ion exchangers has been used for treating waste containing TRU nuclides, relatively high beta and gamma nuclides and high concentrated nitric acid.

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