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THE LABORATORY-SCALE METHOD FOR DECONTAMINATING AND EVAPORATING ALPHA-BEARING AQUEOUS WASTE

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The laboratory-scale method for decontaminating and evaporating alpha-bearing aqueous waste

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Miscellaneous aqueous waste containing Pu and Am is disposed of by converting it into a solid. Prior to the solidification, the waste is decontaminated and evaporated.

Decontamination: Pu and Am are dissolved with various kinds of chemical species of Pu(III), Pu(IV), Pu(VI) and Am(III). When the solution is made alkaline by $Ca(OH)_2$ or NaOH, Pu(III), Pu(IV) and Am(III) precipitate as the hydroxides. Pu(VI) frequently remains in the alkaline because it is amphoteric. The oxidation states of Pu were studied in alkaline solution. Pu(VI) is immediately reduced to Pu(IV) by H_2O_2 at room temperature, while the hydroxide of Pu(III) is turned to that of Pu(IV) with the reagent. An aqueous waste is made alkaline with $Ca(OH)_2$. Then, 30 % H_2O_2 water is added in 20 ml per liter of the solution in order to adjust the Pu oxidation states to Pu(IV), when a small quantity of CaO_2 forms in the solution and carries the trace amounts of Pu(IV) and Am(III) which are still in the solution. In the case of an alkaline solution added NaOH, 30 % H_2O_2 water and 0.01 M Fe(III) solution are added (each 20 ml/l), respectively. The fresh precipitate $Fe(OH)_3$ scavenges the solution. An aqueous waste is thus made

alkaline with $Ca(OH)_2$ (or NaOH), and then H_2O_2-water (and Fe(III)-solution) is added to it. The alkaline supernatant is separated from the precipitate by decantation after standing. Both the precipitation techniques are applied to decontaminate the solution containing trace to sizable amounts of Pu and Am. The initial solution generally contains about 10 mCi/l of α-radioactivity, and an average of 3 μCi/l remains in the processed solution. Recovery of Pu and Am: Pu and Am are concentrated in the small volume of hydroxide slurry. It is dissolved with nitric acid. The resultant solution is a salt solution containing Ca(II) or Na(I), from which Pu and Am are recovered by DBP solvent extraction. From about 200 liters of the aqueous waste, approximately 15 g of Pu and 160 mg of Am are recovered with the overall recovery efficiencies of 85 %.

Evaporation of the alkaline solution: The solution is evaporated with an infrared heater after removal of Pu and Am, when the evaporated water is carried off with air and released to the atmosphere after filtration. Feasibility of the method was demonstrated by evaporating about 400 liters of miscellaneous solution.

アルファ放射性廃液の除染・蒸発法

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（1976年1月30日受理）

Pu，Amを含む雑廃液の除染，Pu，Amの回収，除染廃液処理のための方法を開発した。除染；溶液中でPuはPu（Ⅲ），Pu（Ⅳ），Pu（Ⅵ）で溶け，AmはAm（Ⅲ）で溶けている。液性に左右されない方法として沈殿法を検討した。Ca（OH）$_2$またはNaOHでアルカリ性とすると，Pu（Ⅲ），Pu（Ⅳ），Am（Ⅲ）は水酸化物の沈殿となる。Pu（Ⅵ）の水酸化物は両性のため，しばしば溶液に残る。アルカリ性溶液中でのPuの酸化還元について検討すると，Pu（Ⅵ）は常温で過酸化水素によって直ちにPu（Ⅳ）となる。またこのとき，Pu（Ⅲ）の水酸化物はPu（Ⅳ）のそれにかわる。したがって，廃液をCa（OH）$_2$でアルカリ性として30％の過酸化水素（20$^{m\ell}/_{\ell}$）を加える。このとき，溶液中に少量のCaO_2が生成して，溶液に残存するトレース量のPu（Ⅳ），Am（Ⅲ）を捕集する。廃液をNaOHでアルカリ性とした場合，過酸化水素と0.01M Fe（Ⅲ）溶液（20$^{m\ell}/_{\ell}$）を加える。生成したFe（OH）$_3$がトレース量のPu（Ⅳ），Am（Ⅲ）を捕集する。沈殿と上澄液を分離すると，上澄液はアルファ放射能で約$^{1}/_{10^4}$に除染され，～$10^{-3}\mu Ci/cm^3$となる。本法は溶液の種類，Pu，Amの濃度に左右されずに除染できる。Pu，Amの回収；水酸化物のスラリー状で得たPu，Amは溶媒抽出法で回収する。スラリーに硝酸を加え，沈殿を溶解すると，溶液はCa（Ⅱ）またはNa（Ⅰ）の塩溶液である。この溶液から，DBP抽出によってPu，Amを回収する。約200ℓの廃液を処理してPu，Amを回収した。Pu，Amともに約85％の収率で，それぞれ15g，160mgを得た。本法は廃液の取扱い量にくらべて，回収作業は小さいスケールで行なうことができる。除染廃液の処理；溶液は赤外線蒸発によって減容する。蒸発水は復水せず，グローブボックスの換気々流にのせ，フィルターろ過したのち，大気中に放出する。約400ℓを処理して方法を確立した。

Pu，Amの環境への漏えいは実質的にはゆるされない。処理効果が大きいことが必要であるが，処理中および処理後の安全性が優先する。本法では実験室からでるすべての廃液の除染が可能である。また蒸発減容後残査は固化するが，大部分のPu，Amは除去しているので，固化体のアルファ放射線損傷が軽減される。固化体の塩はカルシウム，ナトリウムの硫酸塩，硝酸塩等で長期保存に適する。本法の除染，蒸発についての確実性，安全性は実廃液の処理で実証した。

CONTENTS

ABSTRACT iv

1. INTRODUCTION 1

2. DECONTAMINATION OF ALPHA-BEARING AQUEOUS WASTES . 4

2.1 OXIDATION STATES OF Pu 5

2.2 COPRECIPITATION WITH $Ca(OH)_2$ AND CaO_2 7

2.3 SCAVENGING EFFECT OF $Fe(OH)_3$ IN ALKALINE SOLUTION 7

3. RECOVERY OF Pu AND Am 10

3.1 SEPARATION FROM $Ca(NO_3)_2$ SOLUTION BY TBP-EXTRACTION 11

3.2 SEPARATION FROM $Ca(NO_3)_2$ OR $NaNO_3$ SOLUTION BY DBP-EXTRACTION 11

4. EVAPORATION AND SOLIDIFICATION OF AQUEOUS WASTES. 12

5. CONCLUSION 16

6. REFERENCES 19

ACKNOWLEDGMENTS 33

FIGURES

1. Influence of salt on α-activity measurement 23

2. Pu-absorption spectra in dilute HNO_3. Reduction of Pu(VI) with H_2O_2 in an alkaline medium 24

3. Pu-absorption spectra in dilute HNO_3 solution. Oxidation of Pu(III) with H_2O_2 in an alkaline medium 25

4. Flowsheet for Pu and Am recovery from α-radioactive aqueous wastes 26

5. Am(III) extraction from Ca- and Na-nitrate solution 27

6. Infrared evaporation system for the treatment of α-radioactive wastes 28

TABLE

1. Scavenging effect of $Fe(OH)_3$ in the NaOH alkaline solution containing Pu or Am 29

2. Scaveging effects of CaO_2 and $Fe(OH)_3$ in alkaline solutions containing Pu and Am 30

3. Results of Pu- and Am-recovery from α-radioactive aqueous wastes 31

4. Alpha radioactive wastes solidified in the evaporation system 32

INTRODUCTION

Alpha-bearing aqueous wastes generated from a Pu handling facility contain appreciable amount of Pu. In the solutions, the element dissolves in some chemical species of Pu(III), Pu(IV) and Pu(VI)[1]∿[5]. Unfortunately, the laboratory aqueous wastes are voluminous and miscellaneous in nature[6]. Under the conditions, the oxidation states of Pu are hardly adjusted to a given state. The recovery of Pu is thus difficult.

The solutions contain also trace amount of ^{241}Am. The nuclide is the disintegration product of ^{241}Pu, that is

$$^{241}\mathrm{Pu} \xrightarrow[14\ \mathrm{y}]{\beta^-} {}^{241}\mathrm{Am} \text{ (Half life 433 y).}$$

Plutonium samples obtained by reprocessing of spent nuclear fuels consist mainly of ^{239}Pu, ^{240}Pu and ^{241}Pu. The content of ^{241}Pu in them is $\lesssim$5 %(wt.). When the samples are used for various experiments, the ^{241}Am is eliminated from them, and thus accumulated in the aqueous wastes. The nuclide dissolves as Am(III) in the solutions.

Plutonium and Am are both harmful and have long-lived α-radioactive nuclides. The aqueous wastes containing them must be stored for a long time. They are kept in a tank, when most amount of Pu must be removed in order to avoid the generation of hydrogen gas. At Dow Chemical Company, the element is removed as Pu-oxalate from miscellaneous aqueous wastes[7]. At Los Alamos Scientific Laboratory, the element has been recovered from the dissolver solutions of Pu alloys, oxides, casting residues, incinerator ashes etc.[8]. Several techniques

were employed historically to recover it: ethyl ether extraction, sodium plutonyl acetate precipitation and TBP solvent extraction. At the present, the recovery is carried out by anion exchange method. After being treated, the solutions are stored in tanks, since ^{241}Am and trace amount of Pu still remain in the solutions. The aqueous wastes, however, are not favorable for a long-term storage. The storage in tanks is considered to be a temporary or interium approach.

It is generally recognized that, after the elimination of Pu and Am, converting the aqueous wastes to a solid is safer and highly desirable(9)(10). For the disposal of aqueous wastes generated from the reprocessing of spent nuclear fuels, Pu, Am and Cm are recovered by solvent extraction(11)∿(15) or ion exchange techniques(16)∿(19). In this case, the solution is of nitric acid. The solution is nearly neutralized and further added $Al(NO_3)_3$ to make a salt solution in order to extract them with TBP extractant(20)∿(23). Ion exchange technique is utilized by denitration of the solution with sugar or formic acid(24)∿(26). For solidification of the solution, Phosphate glass solidification, Spray solidification and Pot solidification systems(27)∿(29) have been developed in large scales. However, a convenient method must be developed for the disposal of the aqueous wastes from a Pu facility, since they are miscellaneous.

In the present work. studies are conducted to the following purposes by use of the aqueous wastes from the Pu handling facility at Japan Atomic Energy Research Institute (JAERI): Decontamination of the solutions for α-radioactivity, Recovery

of Pu and Am, and Evaporation of the decontaminated solutions.

EXPERIMENTAL AND DISCUSSION

1. Analyses

The valency states of Pu were identified in 0.1 M HNO_3 solution with a Shimazu-50L autorecording photometer.

The precipitate, CaO_2 was identified by comparing the X-ray pattern with that represented in ASTM card, No. 3-0862.

Distribution ratio (Kd) of a metal ion in a solvent extraction system is defined as

$$Kd = \frac{\text{Concentration of the metal ion in organic solution}}{\text{Concentration of the metal ion in aqueous solution.}}$$

The amounts of ^{239}Pu and ^{241}Am in the initial aqueous waste were determined by the measurements of the gross α-activity, $I_{Pu} + I_{Am}$, and the activity ratio, I_{Pu}/I_{Am}, obtained from an α-ray energy spectrum, where I_{Pu} and I_{Am} were the activities of Pu and Am, respectively. In this case, α-activity, after mounted on a stainless steel plate, was counted with a 2π gas-flow counter and an α ray-pulse-height analyzer of Si surface barrier type.

Alpha activity in a salt solution was measured by counting the activities of several stainless steel disks on which 0.02 ml aliquots from the solution were mounted, respectively. Fig. 1 shows the influence of salt on α-activity measurement. Both Pu and Am even in a salt solution of 7 M $NaNO_3$ or 3.5 M $Ca(NO_3)_2$ can be determined radiometrically within 15 % error when 0.02 ml aliquot is mounted on a disk (diameter, 2.5 cm). It is necessary to measure several times in order to minimize sampling error.

The decontamination factor (D.F.) of a processed solution

was estimated by

$$D.F. = I_i / I_f ,$$

where I_i and I_f were the gross α-activities in the initial and the final solution, respectively.

2. Decontamination of alpha-bearing aqueous wastes

The main aqueous wastes generated in the facility are as follows.

1) Nitric acid solution; It is the effluent from an anion exchange resin column when a Pu sample is purified with the column. The acidity is about 7 M. The solution contains ∿3 mg/l of Am and a small amount of Pu.
2) Miscellaneous solutions containing H_2SO_4, H_3PO_4 and $HClO_4$; These are generated when Pu in many samples are determined. The acidity is about 1 M. The solutions contain Fe(III), V(IV), Cr(III), Cr(VI), Mn(II), Mo(VI) and chelating reagents such as arsenazo III. They contain also about 0.1 g/l of Pu.
3) Sodium nitrate solution; It is generated when Pu is purified by the precipitation technique.
4) Water; The waste occurs when tools, instrument, etc. are washed or cooled with water.

These solutions contain generally about 10 mCi/l of α-activity. When the solutions are converted into solid waste, it is desirable that the volume of waste is reduced to less than 1/10 that of the initial solution. In order to keep α-activity

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in the solidified waste ∿μCi/l, the aqueous wastes must be scavenged to $<1/10^3$ for α-activity. The aqueous wastes contain HNO_3, H_2SO_4, $HClO_4$ and many metal ions. It is, thus, difficult to aquire a high scavenging effect by solvent extraction and ion exchange techniques.

As one of chemical treatments for elimination of Pu and Am, precipitation method is often applied to the various kinds of waste solution. Most of Pu(III), Pu(IV) and Am(III) can be removed as hydroxides from the aqueous wastes by making them alkaline. Pu(VI) hydroxide has a few chemical species in alkaline solution: $[PuO_2(OH)_2]^0$, $[PuO_2(OH)_3]^-$, $[(PuO_2)_2(OH)_5]^-$. The first, forming in a solution of pH 7.5 ∿ 8.25, is insoluble (solubility product, 1.8×10^{-25})[30]. The others are predominant and soluble in a solution of pH > 8.3. To precipitate Pu(VI) in a solution as hydroxide, the solution must be adjusted the pH to the range of 7.5 ∿ 8.25[45]. It is, thus, advantageous to reduce Pu(VI) in an aqueous waste to Pu(IV) or Pu(III).

Sodium hydroxide or calcium hydroxide is used for neutralization of the acids in the aqueous wastes. After removal of Pu and Am, and volume reduction of the aqueous wastes, the wastes are converted into solid waste as the final process. The Ca- and Na-salts in the solidified waste might be stable in storage for long periods of time.

2.1 Oxidation states of Pu

When a Pu-sample is purified with an anion exchange resin column, Pu(IV) is adsorbed on the column from 7 M HNO_3 solution.

However, Pu(VI), if present, is washed out with the solution. Thus, Pu is often dissolved as Pu(VI) in aqueous wastes, which is a stable state in the solution. In order to reduce Pu(VI) to Pu(IV) in the 7 M HNO_3 solution, the solution must be allowed to stand overnight in the presence of 3 % H_2O_2[31][32]. Generally, the oxidation and reduction of Pu, that is, the valency wandering may occur in aqueous wastes. Unfortunately, the adjustment of its oxidation states is difficult, since the aqueous wastes are miscellaneous and of different acidities. From this reason, the aqueous wastes are made alkaline without adjusting the oxidation states of Pu to a desired state. Pu(III) and Pu(IV) will be fixed as hydroxides in the alkaline solution, while most of Pu(VI) will remain in the solution. There are few oxidizing and reducing agents reported for the ion in the alkaline media. Attention is thus focussed on oxidation or reduction of Pu-ions in ∿0.1 M NaOH solutions. The 0.5 M HNO_3 solution containing Pu(VI) was made alkaline by adding 1 M NaOH. To the alkaline solution, 30 % H_2O_2 was added to make 0.6% solution. After standing for 0.25 or 3 minutes at room temperature (23∿25°C), the solution was acidified with HNO_3 to obtain the 0.1 M HNO_3 solution. The Pu-valency states were determined photometrically[33]. Fig. 2 shows that Pu(VI) has been completely reduced to Pu(IV) in the alkaline solution by standing for 3 minutes. Pu(III) was also studied under the same conditions. In the alkaline medium, Pu(III) is in hydroxide, but it is oxidized instantly to Pu(IV) with H_2O_2, as seen in Fig. 3. Therefore, Pu-ions can be adjusted to Pu(IV) in the

alkaline medium only by adding H_2O_2.

2.2 Coprecipitation with $Ca(OH)_2$ and CaO_2

Approximately 30 liters of ∿7 M HNO_3 solution containing Pu and Am were scavenged. The experiment is designated as Run I. The solution was made alkaline by adding an excess of $Ca(OH)_2$ powder. Fresh precipitate of $Ca(OH)_2$ forms in the solution because of its low solubility. After standing for several minutes, the alkaline supernatant solution was separated by decantation: Solution I and Precipitate I. Solution I was allowed to stand overnight in the presence of 1 % H_2O_2. About 4 g of CaO_2 precipitated per liter of Solution I[34]. The supernatant solution was separated from the precipitate by decantation: Solution II and Precipitate II.

The gross α-activity in the initial HNO_3 solution is ∿9 mCi/l, while the Solutions I and II are ∿100 and ∿10 μCi/l, respectively, as shown in Table 2, Run I. Decontamination factors (D.F.) of Solutions I and II are ∿90 and ∿10^3, respectively.

The aqueous waste can thus be scavenged for α-activity by the two steps. Most of the activity is removed along with the precipitate of $Ca(OH)_2$. The rest coprecipitates with CaO_2, when the oxidation states of Pu are possibly adjusted to Pu(IV).

2.3 Scavenging effect of $Fe(OH)_3$ in alkaline solution

When sodium hydroxide is used for the neutralization of acid in the aqueous wastes, the reagent does not act as the

carrier of Pu and Am like $Ca(OH)_2$ because of its high solubility. Other carrier is required to scavenge the solutions[35][36]. Some aqueous wastes contain weighable amounts of Pu and Am. Most of them will be precipitated as the hydroxides when the solution is made alkaline. Trace amounts will remain in the alkaline solution, however. In order to enhance the fixation process, the coprecipitation technique with Fe(III) was used in the present experiment. It is necessary for eliminating metal ions that the amount of a carrier should be greater than those of the ions to be carried. However, one of the important factors for the treatment of precipitates is to keep the amount of the carrier as small as possible. Here, the coprecipitation technique was applied to scavenging the alkaline solution after most of Pu and Am had been precipitated as hydroxides.

The scavenging effects of Fe(III) carrier were studied in the alkaline media for Am(III), Pu(III), Pu(IV) and Pu(VI). Four 0.1 M HNO_3 solutions containing the respective elements were converted to ∿0.1 M NaOH solutions by adding 1 M NaOH. Then, 20 ml portions of 0.01 M $FeCl_3$ solution were added to one liter fractions of the alkaline solutions, respectively. The solutions were allowed to stand overnight. In Table 1, the D.F.-values for the four supernatant solutions are compared with those without use of the Fe-carrier. The carrier is effective for scavenging Am(III), Pu(III) and Pu(IV) in the alkaline medium (D.F.-value, $\sim 10^3$). On the other hand, it is hardly effective for scavenging Pu(VI), (D.F.-value, ∿2). The alkaline solution containing Pu(VI) was thus allowed to stand

for another 30 minutes after additon of 30 % H_2O_2 (20 ml/l). D.F.-value of the supernatant solution was improved to $\sim 10^3$ by addition of Fe-carrier.

On the basis of the preliminary experiments described, a procedure was devised for fixation of Pu and Am in the aqueous waste. The flowsheet is shown schematically in Fig. 4. A 5-liter fraction of the aqueous waste is made alkaline with NaOH in a tub (pH > 7). Then, 30 % H_2O_2 (20 ml/l) and 0.01 M $FeCl_3$ solution (20 ml/l) are added. After the batch has been stood for several minutes, most of the supernatant solution is poured into a decanter leaving the precipitate in the tub. Several fractions are treated in the same way. After being allowed to stand for about 5 hours, the mixed supernatant solution is decanted to an evaporator described in Section 4.

The procedure was applied to the decontamination of some aqueous wastes containing about 7 mCi/l of α-activity. The obtained results are summarized in Table 2, as Runs II, III and IV. The aqueous wastes in Runs II, III and IV contained HNO_3, H_2SO_4 and water, respectively. They were made alkaline with NaOH, and H_2O_2 and Fe-carrier were added. Some aliquots from the alkaline solutions were sampled before adding H_2O_2 and the carrier. It was found from the ratio of Pu/Am in the aliquots that most of the activity in the alkaline solutions were due to that of Pu, regardless of its content in the initial solution. The Pu in the alkaline solutions should be adjusted to Pu(IV) with H_2O_2, and carried with $Fe(OH)_3$. The activity in each Solution I obtained in three runs was reduced to ~ 3 μCi/l. The

D.F.-values of Solutions I were estimated to be $\sim 10^3$.

The aqueous wastes can be decontaminated with a small quantity of the carrier, regardless of the initial quantities of Pu and Am. After decantation of the supernatant solution, the Pu and Am are recovered from the slurry obtained. The Pu in the slurry is adjusted to Pu(IV) with H_2O_2, which makes the recovery processes of Pu easy.

3. Recovery of Pu and Am

Plutonium(IV) and Am(III) are recovered from the slurry obtained in the flowsheet of Fig. 4. If it is necessary to remove sulfate ions, the slurry is dissolved with 7 M HNO_3 and again made alkaline with NaOH or $Ca(OH)_2$. The fresh precipitate is dissolved by adding 7 M HNO_3 to make an acid solution of <0.3 M. The resultant solution is a salt solution of $NaNO_3$ or $Ca(NO_3)_2$. The Pu(IV) and Am(III) are separated from the large amounts of impurities in the salt solution by batch solvent extraction with 50 % TBP-dodecane or 30 % DBP-dodecane solution (Di(n-butyl)phosphoric acid).

The extraction behavior of Am(III) in the systems of TBP(or DBP)-$Ca(NO_3)_2$ and DBP-$NaNO_3$ are shown in Fig. 5. Am(III) is readily extracted with both extractants from the aqueous salt solutions containing <0.3 M HNO_3. Pu(IV) is also extractable from the nitrate salt solutions in the systems[37][38].

The Pu(IV) and Am(III) extracted are stripped with 1 M HNO_3 solution containing 0.05 M ferrous sulfamate. The Pu(III) in the crude product is separated from the Am(III) by an ion

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exchange technique, after it is adjusted to Pu(IV) with $NaNO_2$. Acidity of the crude product solution is made about 7 M by adding concentrated HNO_3. The resultant solution is poured onto an anion exchange resin column. The Pu(IV) is thus separated from Am(III). The Am(III) in the effluent from the column is coprecipitated with $Fe(OH)_3$. The precipitate is dissolved in dilute HNO_3 solution, which is poured onto a cation exchange resin column. The column is washed with 0.01 M oxalic acid solution to remove Fe(III). The Am(III) is eluted with 3.5 M HNO_3 solution.

3.1 Separation from $Ca(NO_3)_2$ solution by TBP-extraction

Plutonium and Am were extracted with 50 % TBP-dodecane in Run V. The yields were about 90 % for Am but 60 % for Pu, as shown in Table 3. For the extraction of Am(III) from the salt solution, the use of such a high concentration of TBP was necessary to obtain a recovery efficiency of >90 % in a single extraction when the organic solution was contacted with an equal volume of aqueous solution. It was, however, difficult to reduce Pu(IV) in 50% TBP-dodecane solution to Pu(III) with 0.05 M Fe(II)-sulfamate aqueous solution. Another problem was the phase separation. After being contacted, the organic solution separated hardly from the aqueous solution in the extraction system.

3.2 Separation from $Ca(NO_3)_2$ or $NaNO_3$ solution by DBP-extraction

Run VI was carried out in the 30 % DBP dodecane-$Ca(NO_3)_2$

system. The yields of Pu and Am were about 85 %, respectively. In Run VII, the elements were recovered from an aqueous waste containing H_2SO_4, H_3PO_4 and $HClO_4$. In this case, the reagent NaOH was used for neutralization of the acids. The obtained slurry might contain various salts. After removal of the sulfate and phosphate as described, the slurry was acidified with HNO_3. The resultant salt solution was of $NaNO_3$, from which Pu and Am were extracted with DBP-dodecane. The yields of the elements were both approximately 87 %, respectively.

Generally, the Pu and Am in the aqueous wastes must be separated from large amounts of metal ions and other contaminants. Furthermore, some amounts of Fe(III) ion and other substances are brought into the precipitate because large amount of an alkaline reagent is used for neutralization of the acids in the waste solution. The reagent, especially $Ca(OH)_2$ powder contains considerable amounts of impurities, even if it is of reagent grade. Unfortunately, some of them are insoluble in a dilute acid solution. They must be removed before extraction of Pu and Am.

Approximately 15 g of Pu and 160 mg of Am were recovered from about 200 liters of the aqueous wastes treated in Runs I ∿ VII.

4. Evaporation and solidification of aqueous wastes

Radioactive sewages are usually distilled for disposal by boiling[39]∿[41]. Difficulty in this case is control of the forming which causes generation of the mist[42]. When the mist

system. The yields of Pu and Am were about 85 %, respectively. In Run VII, the elements were recovered from an aqueous waste containing H_2SO_4, H_3PO_4 and $HClO_4$. In this case, the reagent NaOH was used for neutralization of the acids. The obtained slurry might contain various salts. After removal of the sulfate and phosphate as described, the slurry was acidified with HNO_3. The resultant salt solution was of $NaNO_3$, from which Pu and Am were extracted with DBP-dodecane. The yields of the elements were both approximately 87 %, respectively.

Generally, the Pu and Am in the aqueous wastes must be separated from large amounts of metal ions and other contaminants. Furthermore, some amounts of Fe(III) ion and other substances are brought into the precipitate because large amount of an alkaline reagent is used for neutralization of the acids in the waste solution. The reagent, especially $Ca(OH)_2$ powder contains considerable amounts of impurities, even if it is of reagent grade. Unfortunately, some of them are insoluble in a dilute acid solution. They must be removed before extraction of Pu and Am.

Approximately 15 g of Pu and 160 mg of Am were recovered from about 200 liters of the aqueous wastes treated in Runs I∿VII.

4. Evaporation and solidification of aqueous wastes

Radioactive sewages are usually distilled for disposal by boiling[39]∿[41]. Difficulty in this case is control of the forming which causes generation of the mist[42]. When the mist

occurs in an evaporator, the distilled water is contaminated with radioactive substances. The permissible levels for α-radioactive waters are so low that extreme cautions must be paid for distillation of the aqueous wastes.

Alpha radioactive aqueous wastes must be treated in the limited space of a glove box. When the wastes are distilled for volume reduction in the glove box, the same volume of distilled water as the original waste is produced in the box. Thus, a new problem occurs to dispose the water. A simple method is proporsed. That is, the water vapor from an evaporator is not condensed but carried off with air.

The simple evaporator made of steel is installed in a glove box as shown schematically in Fig. 6. A 30-liter fraction of the alkaline aqueous waste is fed to the evaporator and checked with pH test paper (pH > 7). It is then heated day and night with infrared heaters set on the ceiling of the top cover. The water vapor carried in the ventilating air of the glove box is filtered by steel-wool prefilter and high efficiency particulate air filters, I and II (H.E.P.A.), and led to the main duct of facility. A dust monitor is set at outlet of the filter box I for continuous check of α-activity. About 30 m^3/hr. of air are ventilated through this route.

About 400 liters of various aqueous wastes were treated in the evaporation system. The results are shown in Table 4. The aqueous wastes evaporated in Runs VIII and IX contained about 2 mCi/l of α-activity, while the aqueous wastes treated in Runs X and XI were decontaminated to <0.1 mCi/l, before the

evaporation. After evaporation, salts remained in the evaporator. They appeared to be the viscous solution of $Ca(NO_3)_2$, the cake of $CaSO_4$, the paste of $NaNO_3$ and the conglomerate of sodium phosphate. The residue was transferred as slurry to a polyethylene waste vessel with a ladle, and mixed with the equal volume of anhydrous gypsum. The mixture was allowed to stand for one night to convert it into a solid waste. The volume of the solidified waste was I/10 ∿ 1/5 of the original solution.

The water evaporated in the apparatus was carried off with air passing over the surface of the aqueous waste at rate of 30 m^3 per hour. The air was heated to about 50 °C at outlet of the glove box. Therefore, it was expected that the ventilating air would carry 1.8 liters of water an hour[43]. The aqueous wastes were evaporated in the system at the rate of 30 liters per two days, that was 0.6 liters per hour. During the evaporation, no condensed water was observed in the air-filter boxes, even in rainy seasons.

Several devices were necessary to treat the radioactive aqueous wastes safely. Corrosion of the ducts in the Pu handling facility and chemical explosions in the glove box were prevented by evaporating in alkaline media. Even hydrochloric acid and perchloric acid solutions could be treated in the system. Bumping of a salt was prevented by heating over the solution in the evaporator. Another problem was the generation of a mist. The degree of mist formation which occurred in the evaporator was judged from the α-radioactive contamination of several stainless steel disks hung in the evaporator. These

were measured for α-activity, after hanging for a week. Usage of infrared lamps caused generation of a mist and sublimation of a salt because the surface of solution might be partly overheated in the evaporator. Thus, six electric resistance heaters sheathed with quartz tubes (total, one kilowatts) were set on the whole ceiling of top cover; radioactivities on the disks hung in Run VIII were on an average 1.2×10^{-4} μCi/cm^2. Ventilating air of the glove box was filtered with filter boxes I and II, successively and led to the main duct. The dust monitor set at outlet of the filter box I indicated that α-activity in the ventilating air was $<4 \times 10^{-12}$ μCi·hr/cm^3 which is the minimum detection limit of the monitor. The activity in the air was estimated to be $\sim 10^{-15}$ μCi/cm^3 after the filter paper of the dust monitor was allowed 3 days to stand for the disintegration of radon and measured for α-activity. After 200 liters of aqueous wastes had been evaporated, the filter box II was dismantled and surveyed for α-activity; no activity was observed in the filter paper (the limiting value was 5 dpm for the measurement of α-activity by 2π gas-flow counting).

The residue had to be removed from the evaporator at the end of the evaporation. In order to keep the apparatus clean, the inner walls were coated with polytetrafluoroethylene, Teflon. Furthermore, four concave parts were made in the floor. They were useful for removal of the residue.

During 2 years, miscellaneous aqueous wastes have been evaporated safely without such trouble as explosion and the contamination of the air released to the atmosphere. The residual

sludge of salts, after evaporation, is solidified with anhydrous gypsum[44]. Weighable quantities of Pu and Am are removed from the resultant sludge, so that the salts in it is not subjected to the α-radiation. The solid wastes were sent to the Desposal Section in JAERI and cemented in waste vessels. The enclosed wastes should be stored virtually forever.

5. CONCLUSION

Aqueous wastes containing Pu(III), Pu(IV), Pu(VI) and Am(III) were decontaminated by precipitation techniques. When the solutions were made alkaline with $Ca(OH)_2$ or NaOH, most amounts of Pu(III), Pu(IV) and Am(III) precipitated as their hydroxides, but Pu(VI) often remained in the solutions, since Pu(VI) is amphoteric and its hydroxide is soluble in a solution of pH >8.3. Oxidation and reduction of Pu were studied in alkaline solution. Pu(VI) could be instantly reduced to Pu(IV) at room temperature in alkaline solution containing dilute H_2O_2. Pu(III) precipitates as hydroxide in alkaline solution, though it could be immediately oxidized to Pu(IV) by the same conditions. Hence, the oxidation states of Pu are adjusted to that of Pu(IV) in alkaline solution by adding H_2O_2. Two coprecipitation techniques were developed, in order to scavenge trace amounts of Pu(IV) and Am(III) in alkaline solution containing $Ca(OH)_2$ or NaOH; To an alkaline solution containing $Ca(OH)_2$, a small amount of 30 % H_2O_2 was added (20 ml/l) to adjust oxidation states of Pu to Pu(IV), when CaO_2 precipitated at the rate of ∿4 g per liter.

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The precipitate was effective as carrier for Pu(IV) and Am(III). In the case of NaOH solution, 30 % H_2O_2 and 0.01 M $FeCl_3$ solutions were added at the rate of 20 ml per liter of a solution to be decontaminated, respectively. The precipitate of $Fe(OH)_3$ formed gradually in the alkaline solution and scavenged the solution. Hence, a fraction of aqueous wastes was made alkaline to make hydroxides of Pu and Am, and decontaminated in the batch by adding H_2O_2 (and dilute $FeCl_3$ solution). The solution could be decontaminated up to low level by standing, regardless of the initial amounts of Pu and Am. The α-bearing aqueous wastes discarded from the Pu handling laboratory were mainly HNO_3 and H_2SO_4 solutions. About 10 mCi/l of α-activity contained in the initial solution, while on the average 3 μCi/l in the processed solutions.

The decontaminated solution was separated from precipitate by decantation. The precipitate was a slurry of hydroxides. The slurry was dissolved by adding concentrated HNO_3 to make a dilute acid solution ($[H^+] < 0.3$ M). From the solution, Pu(IV) and Am(III) were recovered by DBP solvent extraction. They were separated each other and purified by ion exchange techniques. Approximately 15 g of Pu and 160 mg of Am were successfully recovered from about 200 liters of the aqueous wastes with the overall recovery efficiency of 85 %.

Generally speaking, the aqueous waste containing Pu and Am is stored in tanks unless the Pu and Am are extremely eliminated from it (permissible levels: Pu, 5×10^{-5} μCi/cm^3, Am, 4×10^{-5}). Many difficult problems remain to be solved for disposal of the

aqueous waste, as well as the aqueous waste generated from spent nuclear fuel reprocessing[46]∿[52]. At the present time, solvent extraction and ion exchange methods[53]∿[55] are investigated to remove Pu and Am from the aqueous waste of nitric acid, though a satisfactory decontamination for the elements (decontamination factor, 10^4) is not expected by them; Pu dissolves in the solution as Pu(III), Pu(IV) and Pu(VI) having their different behaviors. It forms often polymer or colloid in the solution[56]. Am(III) is less extracted and adsorbed by solvent extraction and ion exchange methods, respectively. The solution is nearly neutralized ($[H^+] \approx 0.1$ M) and made into a salt solution by adding $Al(NO_3)_3$, to enhance the elimination of it[13]. However, some precipitates often form in the low acid solution and carry a part of Am value. In the case of solvent extraction, an emulsification is caused in the aqueous solution by contacting it with an organic solution since the acidity is low. The fact is a severe problem for the treatment of volumenous solution.

It is considered to be very difficult that solvent extraction and ion exchange methods are applied to the decontamination of miscellaneous solutions for the removal of Pu and Am. A precipitation method was investigated in the paper. Various kinds of aqueous wastes can be decontaminated by the method of low level ($\sim 10^{-3}$ μCi/cm^3), regardless the contents of Pu and Am. Further, the advantage of it is to be performed on a single process. Pu and Am are concentrated in a small volume of hydroxide slurry. The elements are thus successfully recovered in the scale.

The decontaminated alkaline solutions were evaporated with

infrared heaters in the paper, when the evaporated water was carried off with air and released to the atmosphere by filtering.

In general, high-level radioactive aqueous wastes are evaporated by boiling[57]. The condensed water generated as by-product is still contaminated with the activity. It is decontaminated by ion exchange resin columns. The effluent from the columns can be disposed as low-level aqueous waste. However, a particlar attention for monitaring of radiations, especially of α-radiation is required since any leakages of Pu and Am to the environment are not substantially allowed. In the developed method, the aqueous wastes are evaporated without boiling in order to prevent the generation of mist. The evaporated water is carried off with air and directly disposed by releasing to the atmosphere. The method is ensured by evaporating about 400 liters of miscellaneous solutions.

It is emphasized that the decontamination and evaporation methods developed in the paper are convenient and safe for the disposal of α-bearing aqueous wastes.

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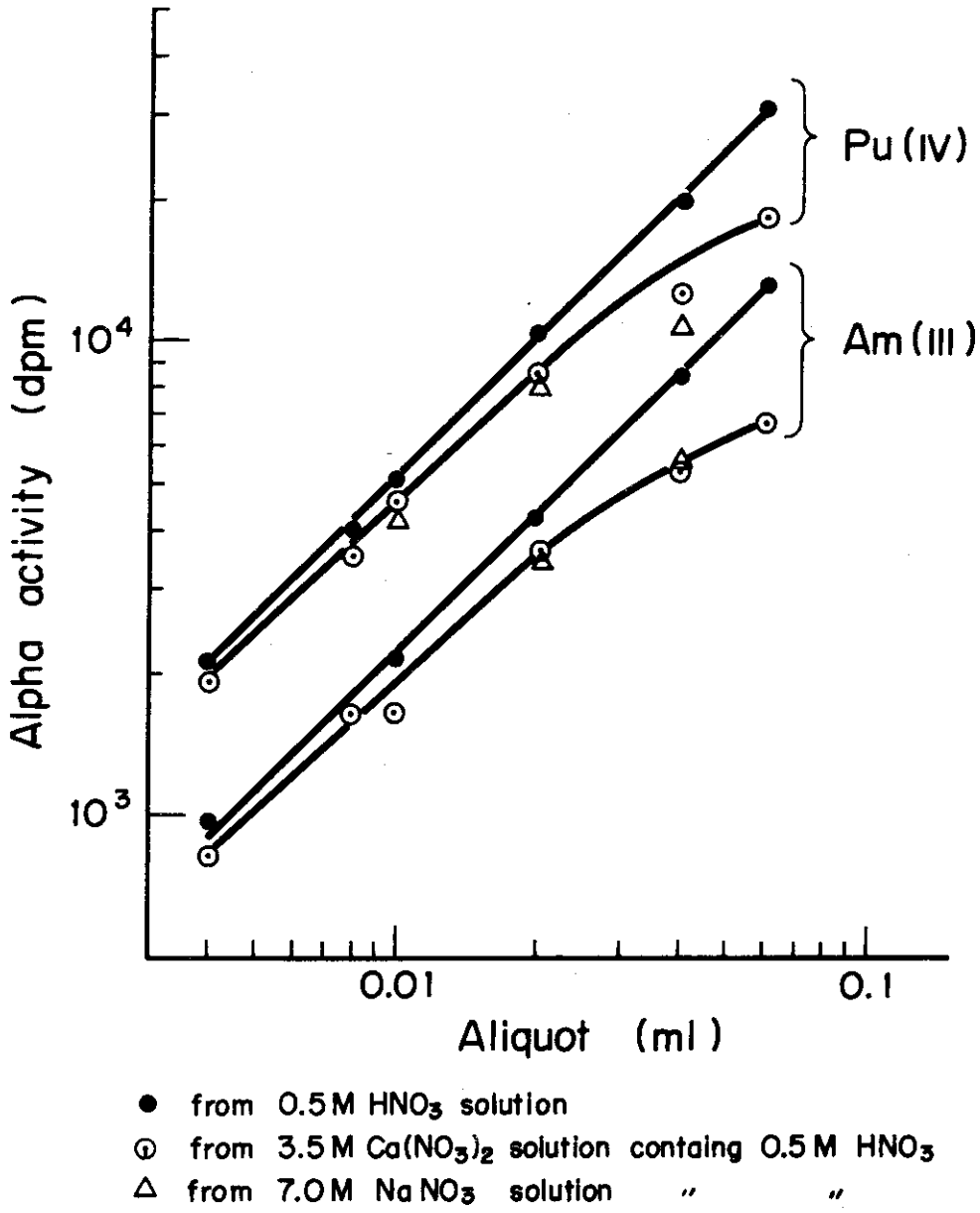


Fig.1 Influence of salt on α-activity measurement; After a series of different aliquots from a solution are mounted on disks, the disks are measured for α-activity.

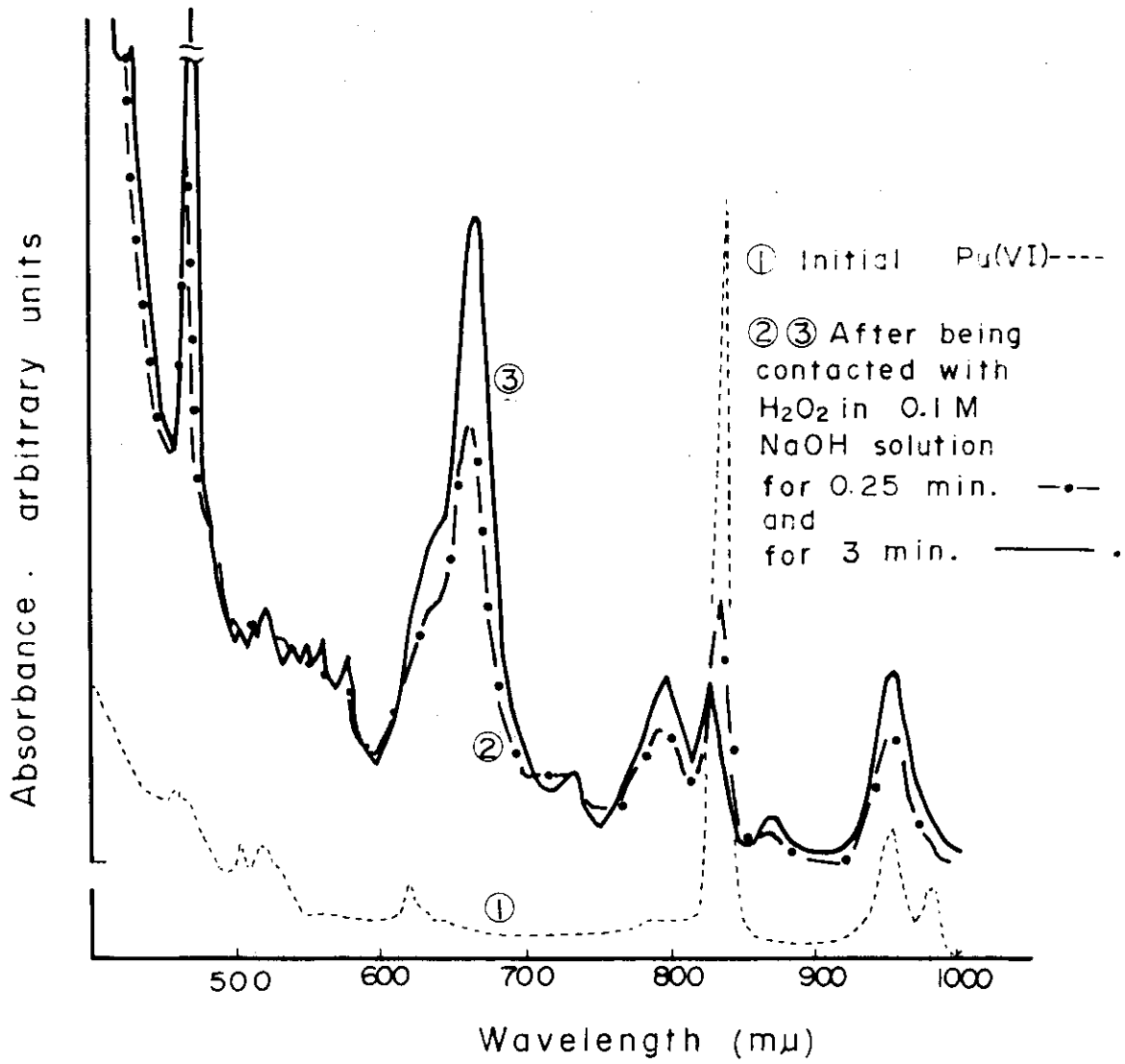


Fig.2 Pu-absorption spectra in dilute HNO_3. Reduction of Pu(VI) with H_2O_2 in an alkaline medium[61]

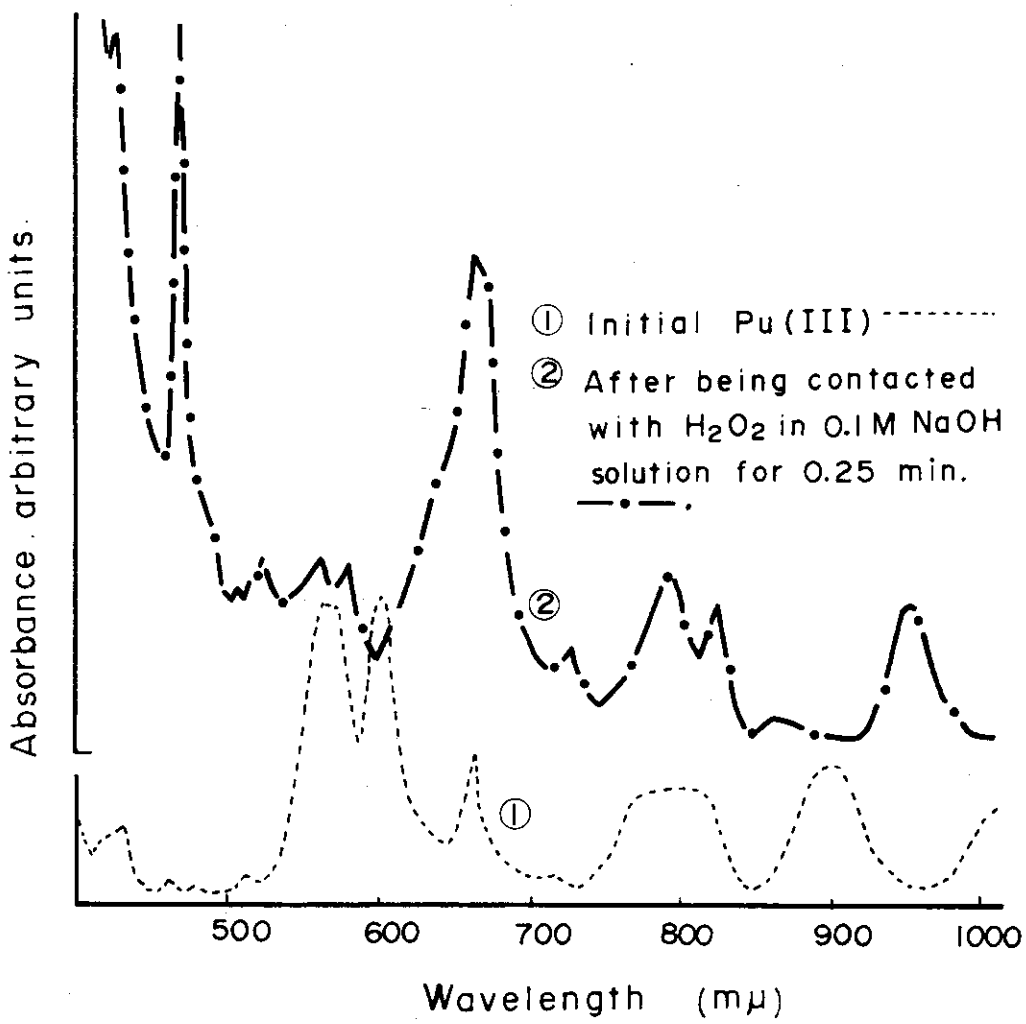


Fig.3 Pu-absorption spectra in dilute HNO_3. Oxidation of Pu(III) with H_2O_2 in an alkaline medium[61]

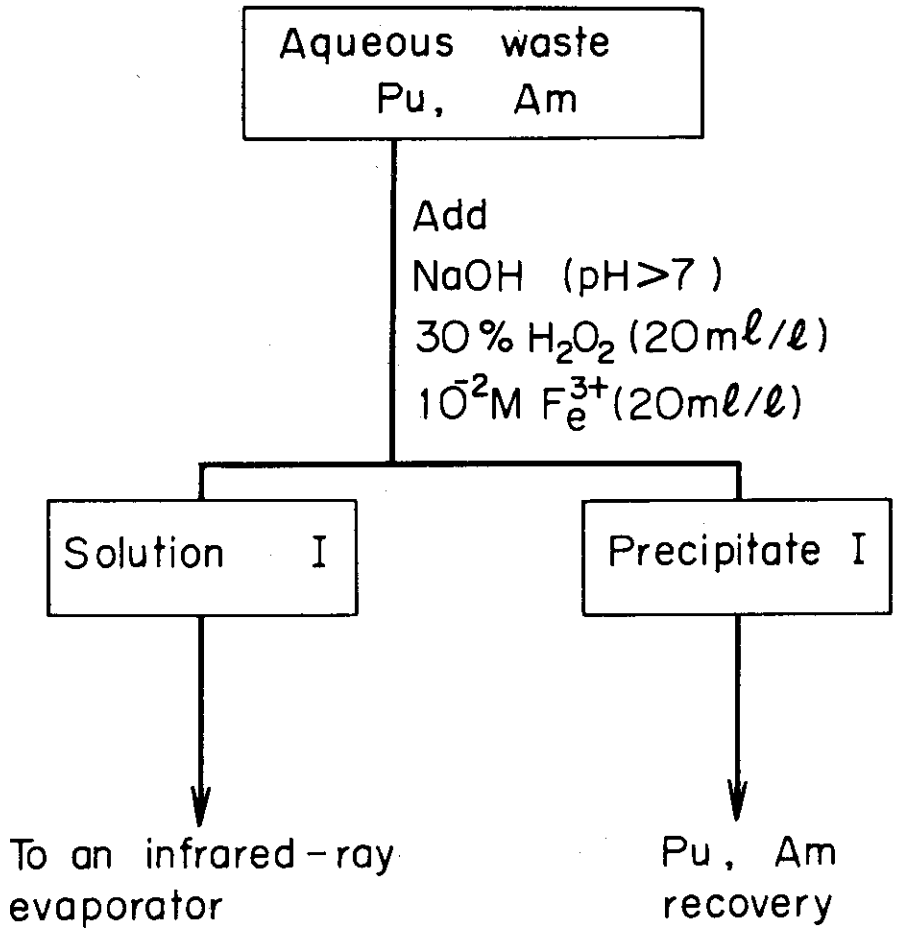
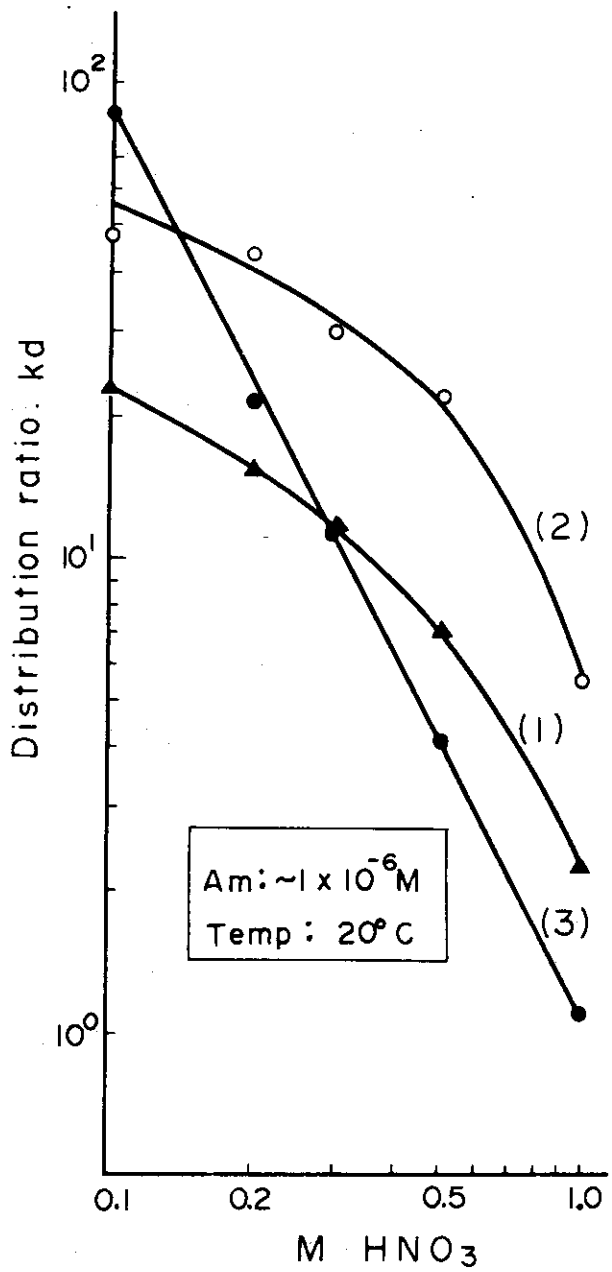


Fig.4 Flowsheet for Pu and Am recovery from α-radioactive aqueous wastes[61]



System :

(1) 50% TBP - $Ca(NO_3)_2$ + HNO_3 (ΣNO_3^-, 6M)

(2) 30% DBP - the same above

(3) 30% DBP - $NaNO_3$ + HNO_3 (ΣNO_3^-, 6M)
(dodecane)

Fig.5 Am(III) extraction from Ca- and Na-nitrate solutions[60]

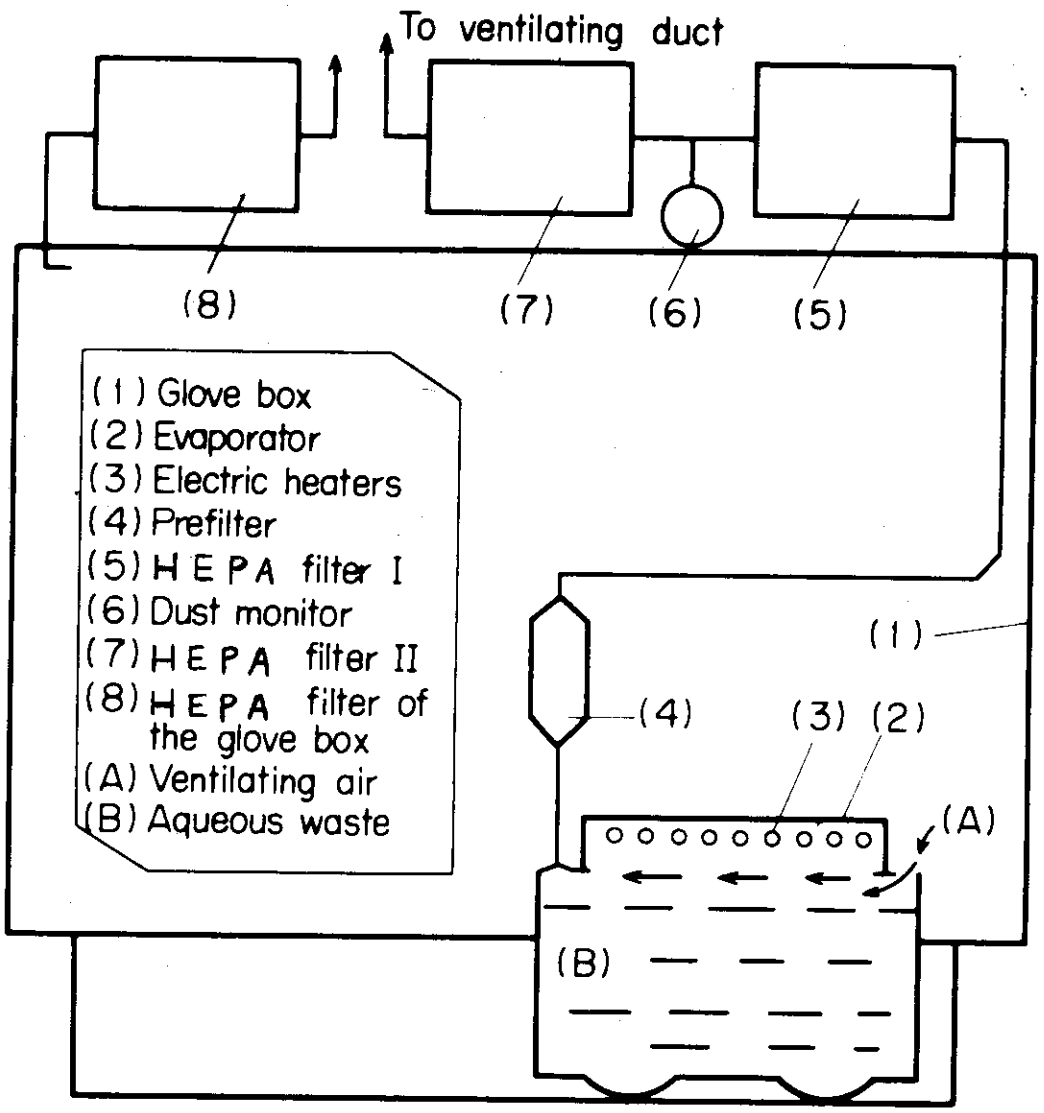


Fig.6 Infrared evaporating system for the treatment of α radioactive wastes[59]

Table 1 Scavenging effect of $Fe(OH)_3$ in the NaOH alkaline solution containing Pu or Am[61]

No.	Conditions		D.F. value of the supernatant solution			
	Initial	Final*	Am(III) 4×10^{-6}M	Pu(III) 2.2×10^{-4}M	Pu(IV) 2.8×10^{-4}M	Pu(VI) 3.6×10^{-4}M
1	0.1 M HNO_3	~0.1 M NaOH	$(1.7\pm0.3)\times10$	$(1.5\pm0.4)\times10^2$	$(2.8\pm1.6)\times10^2$	1.18 ± 0.03
2	〃	~0.1 M NaOH 10^{-2}M $FeCl_3$(20ml/l)	$(1.8\pm0.5)\times10^3$	$(1.7\pm1.0)\times10^3$	$(1.5\pm1.1)\times10^3$	1.54 ± 0.05
3	〃	~ 0.1 M NaOH 30% H_2O_2(20ml/l) 10^{-2}M $FeCl_3$(20ml/l)	$(1.7\pm1.0)\times10^4$	$(2.4\pm1.8)\times10^4$	$(5.3\pm2.5)\times10^4$	$(9.8\pm1.6)\times10^2$

*: Allowed to stand for one night. Error: Standard deviation of sampling.

Table 2 Scavenging effects of CaO_2 and $Fe(OH)_3$ in alkaline solutions containing Pu and Am[58][61]

	Run No.	I	II	III	IV
Initial aqueous waste	Acid	~7 M HNO_3	~7 M HNO_3	~1 M H_2SO_4	Water
	Volume (l)	30	4	50	35
	Gross α (mCi/l)	9.32 ± 0.04	6.3 ± 0.3	7.7 ± 0.3	0.04 ± 0.1
	Pu/Am (α-activity)	0.995	0.170	13.9	6.68
	Pu (total g)	2.27	0.06	5.82	
	Am (total mg)	40.8	6.25	7.49	
Super-natant solution	Reagent added	$Ca(OH)_2$	NaOH	NaOH	NaOH
	(μCi/l)	98.5 ± 0.5	54 ± 5	12 ± 4	
	Pu/Am (α-activity)		8.60	6.67	
	Scavenging with	CaO_2	$Fe(OH)_3$	$Fe(OH)_3$	$Fe(OH)_3$
	(μCi/l)	10.8 ± 0.6	3.6 ± 0.5	2.4 ± 1	0.5 ± 0.5
	D.F. value	8.6×10^2	1.7×10^3	3.2×10^3	1×10^2
Yields*	Pu (g)	1.91	5.9 ± 0.3		
	Pu (%)	84.1	100.3		
	Am (mg)	30.4	12.7 ± 0.3		
	Am (%)	74.4	92.4		

*: The actinides were recovered by ion exchange techniques from the precipitate obtained. Error: Standard deviation of sampling.

Table 3 Results of Pu- and Am-recovery from α-radioactive aqueous wastes[60]

	Run No.	V	VI	VII
Initial aqueous waste	Acid	~7 M HNO_3	~7 M HNO_3	~1 M H_2SO_4
	Volume (l)	21	18	87
	Gross α (mCi/l)	10.8	12.3	5.76
	Pu (g)	0.32	1.12	6.67
	Am (mg)	60.3	44.4	27.1
Decontaminated solution	Reagent added	$Ca(OH)_2$	$Ca(OH)_2$	NaOH
	Gross α (μCi/l)	0.19 ± 0.03	0.28 ± 0.03	1.6 ± 0.9
	D.F. value	5.7×10^4	4.4×10^4	2.6×10^3
Yields of Pu and Am	Extractant (% in dodecane)	50-TBP	30-DBP	30-DBP
	Pu (g)	0.2 ± 0.01	0.91 ± 0.07	5.8 ± 0.2
	(%)	62.5	81.2	87.0
	Am (mg)	55 ± 1	38 ± 1	23 ± 3
	(%)	91.2	86.0	85.0

Table 4 Alpha radioactive wastes solidified in the evaporation system [59]

Run No.	VIII	IX	X	XI
Aqueous waste	H_2SO_4, $HClO_4$ ~1M H^+	$NaNO_3$	HNO_3 ~7M	H_2SO_4, H_3PO_4 ~2M H^+
Gross α (mCi/l)	1.6	1.4	9.8	5.7
Reagent added	$Ca(OH)_2$	—	$Ca(OH)_2$	NaOH
Recovery of Pu and Am	Non	Non	Yes	Yes
Volume (l)	130	50	110	100
Gross α (mCi/l)	1.6	1.4	<0.1	<0.01
State of residue	Cake	Paste	Viscous solution	Conglomerate
Waste solidified with anhydrous gypsum (l)	12	4	22	20
Waste solidified with anhydrous gypsum (kg)	28	8	47	35

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