

## Distillation of cadmium from uranium–plutonium–cadmium alloy

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### Abstract

Uranium–plutonium alloy was prepared by distillation of cadmium from U–Pu–Cd ternary alloy. The initial ternary alloy contained 2.9 wt% U and 8.7 wt% Pu other than Cd, which were recovered by molten salt electrolysis with liquid Cd cathode. The distillation experiments were conducted in 10 g scale of the initial alloy using a small-scale distillation furnace equipped with an evaporator and a condenser in a vacuum vessel. After distillation at 1073 K, the weight of the residue was in good agreement with that of the loaded actinides, where the content of Cd decreased to less than 0.05 wt%. The uranium–plutonium alloy product was recovered without adhering to the yttria crucible. The cross section of the product was observed using electron probe micro-analyzer and it was found to consist of a dense material. Almost all of the evaporated Cd was recovered in the condenser and so enclosed well in the apparatus.

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### 1. Introduction

Central Research Institute of Electric Power Industry (CRIEPI) and Japan Atomic Energy Research Institute (JAERI) have been studying on pyrometallurgical processes for spent metallic and nitride fuels [1,2]. Molten salt electrorefining in eutectic lithium chloride–potas-

sium chloride (LiCl–KCl) is employed for recovering heavy metals (HM), i.e. uranium (U), plutonium (Pu) and minor actinides (MA). Plutonium and minor actinides are recovered into liquid cadmium (Cd) cathode together with U [3–5]. Cadmium in the cathode product is separated by distillation from the recovered HM, prior to the fabrication of recycled fuel.

Under a joint research program between CRIEPI and JAERI, the electrorefining with liquid Cd cathode has been researched using U and Pu [4,5], which are two major constituents recovered into the cathode. The experiments of electrolysis were carried out to

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recover up to 10 wt% of the actinides in the cathode, that is the authors' tentative target for the HM content in the cathode product. Uranium and plutonium were recovered simultaneously at high current efficiencies. At the experimental temperature of 773 K, the liquid Cd phase, in which  $\sim 4$  wt% of the actinides dissolved, coexisted with U–Pu–Cd ternary compounds such as  $\text{MCd}_{11}$  and  $\text{MCd}_6$  ( $M = \text{U}, \text{Pu}$ ).

Following the development of the electrorefining, study on the distillation process has been carried out. The product of the liquid Cd cathode consists mainly of Cd, U and Pu. Their vapor pressures over the respective pure metals are shown in Fig. 1 with respect to reciprocal temperatures together with Cd vapor pressure over  $\text{PuCd}_2$  and Pu mixture [6,7]. In an initial stage of distillation, vapor pressure of Cd is likely to be as high as that over pure Cd, since most part of the cathode, say 90 wt%, is Cd and there would be most probably a liquid Cd. In the progress of evaporation of Cd, the remaining part of Cd would form various U–Pu–Cd intermetallic compounds. Vapor pressure of Cd over these compounds should be lower than that over pure Cd. Intermetallic compound is not shown in the U–Cd binary phase diagram above 750 K [8], but some intermetallic compounds exist in the Pu–Cd binary phase diagram [8]. Nakajima et al. have measured the vapor pressure of Cd over the mixture of Pu and  $\text{PuCd}_2$  [7], which is the most Pu-rich compound in the binary system [8]. Fig. 1 also shows their result, which is lower than that over pure Cd, but still much higher than those of U and Pu. Consequently, the distillation to separate Cd from U–Pu alloy is considered to be feasible. However, neither U–Pu–Cd ternary phase diagram of the U–Pu rich region, nor the solubility of Cd in U and Pu metal each has been reported. Therefore, the distillation experiment with U–Pu–Cd alloy should be carried out to examine the amount of Cd remaining in residual U–Pu alloy.

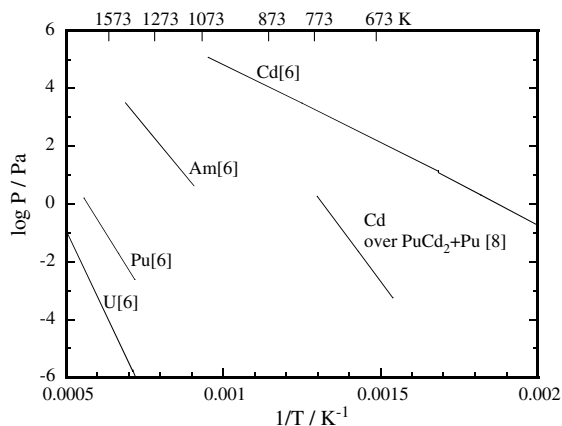


Fig. 1. Vapor pressures of actinides and Cd [6,8].

Since the vapor pressure of Cd decreases in the progress of distillation, a heating procedure should be optimized to avoid HM scattering by violent evaporation in an early stage at the same time to carry out efficient distillation of Cd to prepare Cd-free HM alloy. Another loss of HM by its own oxidation or reaction with crucible material should also be minimized by proper equipment design.

In order to establish mass balance in the distillation process, the behavior of MA, which are recovered into the liquid Cd cathode with U and Pu, should be studied. Americium is one of the important MA elements in the distillation, because Am amounts to  $\sim 70$  wt% of the entire MA in the spent fuel and the vapor pressure of Am is much higher than those of U and Pu as shown in Fig. 1.

In the present work, two kinds of distillation experiments were carried out using a small-scale apparatus. At first, distillation experiments with pure Cd metal were performed to find a condition for gentle evaporation. After that, the distillation experiments using U–Pu–Cd alloy, which was recovered in the previous molten salt electrolysis experiment with the liquid Cd cathode, were conducted to examine the Cd remaining as impurity in the residual alloy and hence to obtain practical information for equipment design and operation conditions. Additionally, evaporation of Am was examined by measuring on Am-241, which is a decay product of Pu-241.

## 2. Experimental

### 2.1. Distillation apparatus

For the research and development of the distillation process, a small-scale distillation apparatus shown in Fig. 2 was designed and installed in an argon atmosphere glove box. The apparatus consists of three sections, which were named evaporator, condenser and bridge. The lowest part is the evaporator, in which Cd is evaporated and residual HM alloy is recovered. The evaporator is equipped with the main heater. A Kanthal Super heating element is used for the main heater, which can be heated up to 1673 K. A primary crucible with maximum 43 mm outer diameter can be contained in the graphite secondary crucible, which is placed in the graphite furnace well of the evaporator. The bridge is the graphite tube sitting on the secondary crucible. The tube is a passage of Cd vapor. The sub-heater, which is a small resistance heater, is placed around the bridge to prevent Cd vapor condensation that causes blocking the passage. Vapor of Cd is condensed and collected on the inner surface of the stainless steel (Type 410) condenser sitting on the bridge. Baffle plates are fitted to the rid of the condenser to make a labyrinth for Cd vapor. The outer vessel is airtight to be evacuated

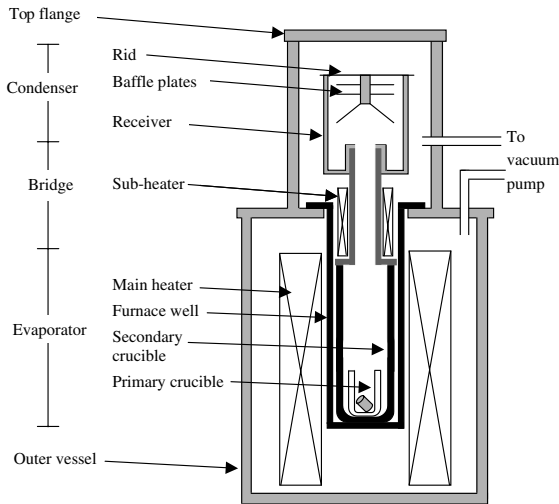


Fig. 2. Schematic view of distillation apparatus.

with a rotary vacuum pump. The evaporator, bridge and condenser are evacuated through a small hole bored in the rid of the condenser. The absolute vacuum pressure reached less than 1 Pa before heating and kept less than 10 Pa even in heating by continuous operation of the pump. The temperature at the evaporator was measured using two thermo-couples that were fitted along the groove on the inside wall of the furnace well. The temperature at the condenser was also measured with a thermo-couple attached on the outside wall of the receiver. The temperature at the bridge was observed using the thermo-couple that controls the sub-heater.

## 2.2. Distillation experiments

The distillation experiments with pure Cd metal were conducted in 10 g scale, which were almost the same as those with U–Pu–Cd alloy described below. Cadmium was heated in vacuum at various temperatures to find an appropriate operation temperature, which is high enough to evaporate 10 g of Cd in a given distillation time. The distillation time of the present work was set for 2 h considering the procedure including heating and cooling to be completed within 1 day. An alumina primary crucible with 12 mm of the inner diameter containing 10 g of Cd was placed in the secondary crucible of the evaporator. After arrangement of all the components, the top flange was shut and then the apparatus was evacuated. The bridge was heated up using the sub-heater prior to the evaporator, at which the temperature was increased so as to chase the temperature at the bridge. Finally, the temperature at the bridge was controlled to the same as that of the evaporator. After the distillation, each component in the apparatus was weighed to examine the material balance, i.e. the amounts of evaporated Cd and deposited Cd.

The distillation experiments of U–Pu–Cd ternary were conducted using the product of the previous molten salt electrolysis [4]. Uranium and plutonium were recovered into the liquid Cd cathode through the molten salt, in which 1.1 wt% U and 4.8 wt% Pu were contained. The content of HM in the alloy was calculated to be 11.6 wt% from the passed charge by assuming current efficiency 100%. The ratio of U/Pu was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to be 1/3.0, which means 2.9 wt% U and 8.7 wt% Pu in the alloy. The observation by electron probe micro-analyzer (EPMA) showed that U and Pu in the alloy formed intermetallic compounds with Cd. The X-ray diffraction (XRD) pattern of the alloy is shown in Fig. 3. The lattices of Cd and  $\text{PuCd}_{11}$  in the JCPDS [9] were identified in the XRD pattern. Americium was also contained by 0.15 wt% in the alloy as a decay product of Pu-241.

The cathode product of 130 g was cut into about 10 g ingot, which was put in an yttria primary crucible with 14 mm of the inner diameter. Distillation experiments in vacuum were carried out with two different heating patterns. In RUN 1, distillation temperature was increased stepwise to examine the decrease of Cd remaining in the HM residue at each temperature. The evaporator was held at each distillation temperature for 2 h, and then cooled down to an ambient temperature to take samples from the residue. Samples were also taken from Cd recovered in the condenser to examine Am evaporation. RUN 2 was a straightforward

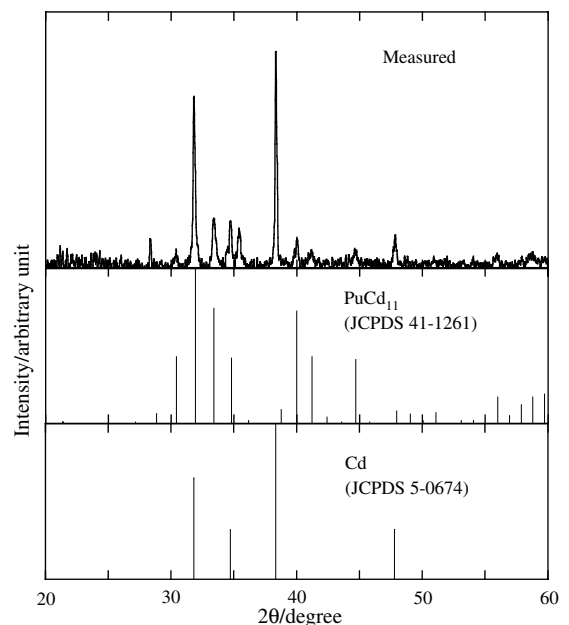


Fig. 3. X-ray diffraction pattern of the initial U–Pu–Cd ternary alloy.

distillation, in which the apparatus was not disassembled until completion of a heating procedure to prepare Cd-free U–Pu alloy. The distillation temperature was determined from the result of RUN 1.

The composition of the U–Pu–Cd ternary was analyzed by ICP-AES, while the oxygen content was by inert gas-fusion coulometry [10]. X-ray diffraction with  $\text{CuK}\alpha$  radiation was conducted to identify phases in the U–Pu–Cd ternary. The product of HM alloy was observed by EPMA. Americium was analyzed by gamma-ray spectrometry using a high-purity germanium detector and a multi channel analyzer.

### 3. Results and discussion

#### 3.1. Distillation experiments with Cd metal

The material balances in the experiments with Cd metal were summarized in Table 1. After the distillations, the primary crucible containing residue was weighed to determine the amount of ‘Remaining Cd’ indicated in Table 1. The secondary crucible, bridge tube, condenser rid and receiver were also weighed with Cd deposition. ‘Total recovered Cd’ in Table 1 is the sum of ‘Remaining Cd’ and ‘Deposited Cd’. In every experiment, ‘Total recovered Cd’ was in good agreement with ‘Loaded Cd’, thus good material balance was obtained.

In the distillation at 673 K, 8.6 g of Cd remained in the primary crucible. Therefore, the distillation temperature of 673 K was too low to evaporate 10 g of Cd metal in the limited time of 2 h. Some of the deposited Cd was observed as frost at the bottom of the bridge and the upper inside wall of the secondary crucible. The amount of the Cd frost was 0.15 g in the total deposited Cd of 1.4 g.

On the other hand, at 723 K and 773 K, 10 g of Cd evaporated completely. Therefore, the distillation temperature of 723 K seems to be high enough for the required evaporation. The vapor of Cd was enclosed well in the apparatus and almost all of the evaporated Cd deposited in the condenser, at which the temperature rose up to around 573 K. No frost of Cd was observed at any other section, thus the temperature of the bridge was controlled appropriately. Fig. 4 shows the deposition of Cd on the baffle plates of the condenser rid.

Table 1  
Material balances in the distillation experiments with Cd metal

Distillation temperature (K)	673	723	773
Loaded Cd/g	10.019	10.028	10.037
Total recovered Cd/g	9.974	10.032	10.011
Remaining Cd/g	8.561	0.002	0.001
Deposited Cd/g	1.413	10.030	10.010



Fig. 4. Cadmium deposit on the baffle plates of the condenser rid.

The vapor of Cd condensed to form a thin film. This material was peeled easily and the condenser could be reused with no further procedure.

#### 3.2. Distillation experiments with U–Pu–Cd alloy

In RUN 1, the U–Pu–Cd alloy was heated at the incremental temperature of 723 K, 873 K, 973 K and 1073 K. The bridge and evaporator were heated up in the same manner as in the pure Cd distillation. Finally, the temperature at the bridge was kept at 723 K, which was high enough to prevent Cd vapor from condensing, except for the distillation at 1073 K. During the distillation at 1073 K, the temperature at the bridge rose up to around 753 K.

The result of RUN 1 is summarized in Table 2 as the weight ratios of the residue to the loaded HM, which was expected from the loaded amount and the HM content of the initial alloy. The table also showed the Cd

Table 2  
Summary of distillation experiment RUN 1 with U–Pu–Cd alloy

Distillation temperature (K)	Initial	723	873	973	1073
Residue/loaded HM wt ratio	8.62	1.39	1.00	1.01	1.02
Cd content by ICP-AES/wt%	88.4 <sup>a</sup>	28.2	0.17	<0.08	N.A.

<sup>a</sup> Calculated value from the passed electric charge in the the molten salt electrolysis in which the initial U–Pu–Cd ternary alloy was obtained.

contents in the residue, which were analyzed by ICP-AES.

In the distillation at 723 K, ~95% of the initial Cd amount evaporated and the Cd content in the residue decreased to 28.2 wt%. X-ray diffraction was conducted to identify phases in the residual U–Pu–Cd ternary. The diffraction pattern shown in Fig. 5(a) is obviously different from that of the initial alloy in Fig. 3. The two intensive peaks in Fig. 5(a) corresponded to the characteristic peaks of  $\text{PuCd}_2$  measured by Nakajima et al. [8], which was shown in Fig. 5(b). These results indicate that the lattices of Cd and  $\text{PuCd}_{11}$  disappeared during the distillation and the Cd remaining in the residue formed the lattice of  $\text{PuCd}_2$ . On the other hand, the lattice of  $\text{PuCd}_2$  must decompose even at 723 K because the molar ratio of Cd/HM in the residue is 0.84 and even Cd/Pu is 1.11, which is smaller than that of  $\text{PuCd}_2$ .

After the distillation at 873 K, almost all of Cd was evaporated and the content of Cd in the residue decreased to 0.17 wt%. The weight of the residue was in good agreement with the expected HM weight, thus Cd seems to be evaporated gently as to avoid HM scattering. After the distillation at 973 K, the Cd content decreased to less than 0.08 wt%. The weight gain of the residue at the higher temperatures, 973 K and 1073 K, would mean the occurrence of oxidation that was suggested by the oxygen analysis as described in the next paragraph. Totally 8.30 g of Cd recovered in the con-

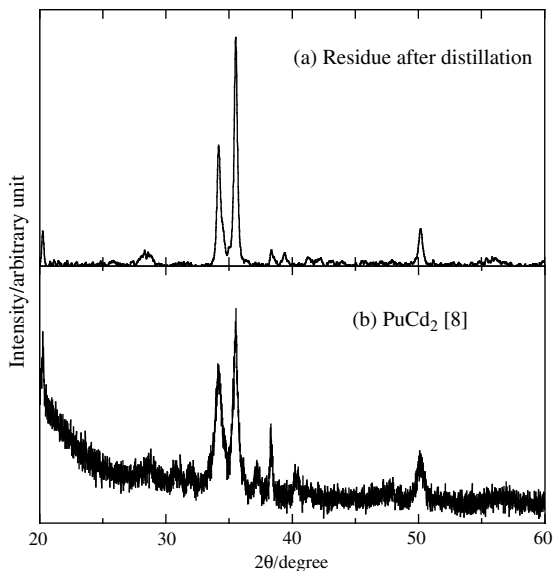


Fig. 5. (a) X-ray diffraction pattern of residue after distillation at 723 K in RUN 1. (b) X-ray diffraction pattern of  $\text{PuCd}_2$  measured by Nakajima et al. [8].

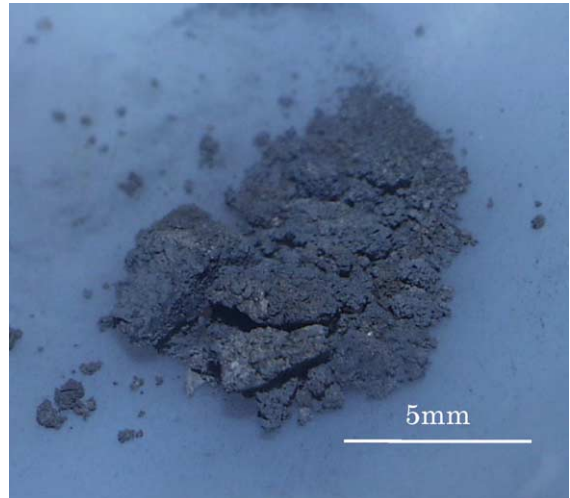


Fig. 6. Residue after distillation at 1073 K in RUN 1.

denser through RUN 1 was consistent with 8.28 g of the weight loss in the evaporator.

Fig. 6 shows the residue after it was heated at 1073 K. The residue did not consolidate in melting, although the temperature of 1073 K is higher than the expected liquidus temperature of the residual U–Pu alloy with the U/Pu ratio of 1/3.0 [11]. Since the oxygen analysis showed that the residue was accompanied with oxygen of 0.5 wt%, it was speculated that the residual U–Pu alloy was covered with oxide layer and prevented from consolidating into a spherical form. Because such powdery and porous material with a low density would not be suitable for the metallic fuel fabrication by the injection casting, distillation procedure should also be optimized to avoid oxidation of the residual HM alloy.

In RUN 2, the vacuum vessel was not opened until the completion of the distillation procedure in order to minimize oxidation of the residual U–Pu alloy. The distillation was conducted in two steps. The first step was the distillation at 723 K to evaporate most of Cd gently. After that, with neither cooling nor opening the apparatus, the temperature at the evaporator was increased up to 1073 K for the second step to remove Cd completely and to melt and consolidate the residual U–Pu product. The holding time in each step was 2 h. Through the heating procedure of RUN 2, the temperature at the bridge was controlled at 723 K as in RUN 1.

Fig. 7 shows the U–Pu product recovered in RUN 2. Some grains in the spherical shape suggest that the U–Pu alloy should melt to consolidate without adhering to the yttria crucible. The weight of the residual HM alloy was 0.670 g, which agreed with 0.667 g expected from the loaded amount and the composition of the initial ternary alloy. The impurity of Cd decreased to less than 0.05 wt% and the oxygen content was ~0.05 wt%





Fig. 7. Residual HM alloy obtained in RUN 2.

in the largest grain shown in Fig. 7. The grain was cut into several pieces to observe the cross section by EPMA. The polished cross section looked shiny and metallic. Fig. 8 is the secondary electron image of the cross section. As no pore was found in the observation, the grain should consist of a dense material. Thus, U–Pu alloy was prepared successfully to be appropriate for the metal fuel fabrication by the injection casting.

The weight of the Cd recovered in the condenser was 5.04 g, which was close to 5.08 g of the weight loss in the evaporator. Even in the distillation at 1073 K, the temperature at the condenser was kept less than 573 K and Cd vapor hardly leaked out of the condenser. The content of Am in the recovered Cd was analyzed by gamma-ray spectrometry to examine Am evaporation.

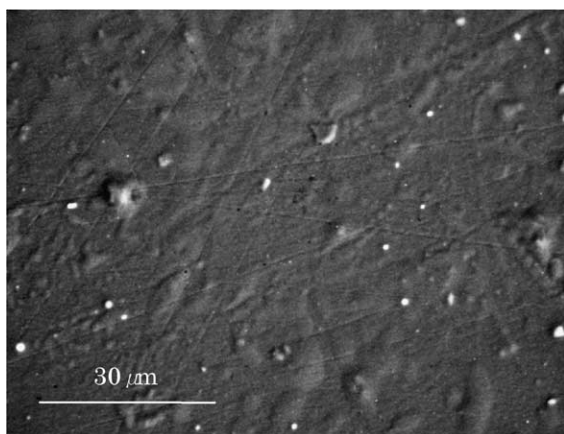


Fig. 8. Cross section of the U–Pu alloy obtained in RUN 2. (secondary electron image).

It corresponded to the background level of Am, which was detected in the Cd deposit recovered in the pure Cd distillation. Since the detected Am was less than 0.01% of the Am amount in the initial U–Pu–Cd alloy loaded, Am evaporation was not notable in the distillation up to 1073 K.

#### 4. Conclusions

Distillation experiments with U–Pu–Cd ternary alloy in 10 g scale were conducted to prepare U–Pu alloy by separating Cd, using a small-scale apparatus equipped with an evaporator and a condenser in a vacuum vessel. The initially obtained ternary alloy contained 2.9 wt% U and 8.7 wt% Pu, which was recovered into the liquid Cd cathode by molten salt electrolysis.

The ternary alloy was heated up stepwise to examine the decrease of Cd remaining in the U–Pu residue. In the distillation at 723 K, ~95% of the initial Cd amount evaporated gently so as to avoid HM scattering and the Cd content in the residue decreased to 28.2 wt%. X-ray diffraction of the U–Pu–Cd ternary residue showed that the remaining Cd formed the lattice of  $\text{PuCd}_2$ . After the distillation at 873 K and 973 K, the content of Cd in the residue decreased to 0.17 wt% and less than 0.08 wt%, respectively. On the other hand, the residual U–Pu alloy was accompanied with oxygen of 0.5 wt% and it did not consolidate in melting after heated up to 1073 K, which is higher than the liquidus temperature expected from the U/Pu ratio.

In the second experiment, the vacuum vessel was not opened until the completion of the stepwise heating procedure at 723 K and 1073 K in order to minimize the oxidation of the U–Pu residue. Consequently, the U–Pu product consolidated in spherical shape and the increase of oxygen contamination was kept to ~0.05 wt% in the U–Pu grains. The observation by EPMA showed that the U–Pu product should consist of a dense material. The impurity of Cd decreased to less than 0.05 wt%, while the weight of the U–Pu product was 0.670 g, which agreed with 0.667 g expected from the composition and the loaded amount of the initial ternary alloy. The yttria crucible was applicable to the distillation experiments and the U–Pu product was recovered without adhering on it.

The vapor of Cd hardly leaked from the condenser, at which the temperature was kept below 573 K. The weight of Cd recovered in the condenser was 5.04 g, which was close to 5.08 g of the weight loss in the evaporator. Evaporation of Am, which was involved as the decay product of Pu-241, was not notable in the distillation up to 1073 K, since the content of Am in the recovered Cd corresponded to the background level of Am, which was detected in the Cd recovered in the pure Cd distillation.

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