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REDUCTANTS IN REPROCESSING

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Separation of Neptunium, Plutonium and Uranium by Using
Butyraldehydes as Reductants in Reprocessing

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A new separation process of Np, Pu and U using n- and iso-butyraldehydes as reductants for Np(VI) and Pu(IV), respectively, in the reprocessing has been investigated.

In the kinetics study of Np, Pu and U reduction, it was found that n-butyraldehyde reduced Np(VI) to Np(V) in the Purex solution but did not reduce Pu(IV) and U(VI), and iso-butyraldehyde reduced Np(VI) and Pu(IV) but did not reduce U(VI). Based on these results, a new selective separation process of Np, Pu and U was proposed. The main process consists of three steps: co-decontamination, Np separation and U/Pu partition steps. In the Np separation step, Np(VI) extracted together with Pu(IV) and U(VI) by the solvent of 30 % tri-n-butyl phosphate/n-dodecane was selectively reduced to Np(V) by using n-butyraldehyde and was back-extracted from the solvent. In the U/Pu partition step, iso-butyraldehyde was used as a reductant for Pu(IV).

The effectiveness of the new process was demonstrated in the flow sheet study using miniature mixer-settlers. In the Np separation step, 99.98 % of Np extracted together with U(VI) in the co-decontamination step was reduced by n-butyraldehyde and separated from U. In the U/Pu partition step, more than 99 % of Pu was reduced by iso-butyraldehyde and separated from U.

Keywords: Separation, Neptunium, Plutonium, Uranium, n-Butyraldehyde, iso-Butyraldehyde, Reduction, Purex Process, Extraction, TBP

ブチルアルデヒド還元剤を用いた再処理抽出工程における
ネプツニウム、プルトニウム及びウランの分離

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(1993年9月9日受理)

還元剤として *n*- 及び *iso*-ブチルアルデヒドを用いた新しいネプツニウム、プルトニウム及びウランの再処理工程分離プロセスに関する研究を行った。

本研究は、Np, Pu 及び U の反応速度測定実験とフローシート実験からなる。反応速度測定実験では、*n*-ブチルアルデヒドはビューレックスプロセス溶液条件下において Np(VI) を Np(V) に還元するが、Pu(IV) 及び U(VI) を還元しないこと、また、*iso*-ブチルアルデヒドは Np(VI) 及び Pu(IV) を還元するが U(VI) を還元しないことがわかった。これらの結果をもとに、共除染工程、Np 分離工程及び U/Pu 分配工程から構成される新しい分離プロセスを提案した。Np 分離工程では、*n*-ブチルアルデヒドを用いて U(VI) 及び Pu(IV) とともに抽出される Np(VI) を選択的に Np(V) に還元する。U/Pu 分配工程では、Pu(IV) の還元剤として *iso*-ブチルアルデヒドを用いる。

提案した新しい分離プロセスの有効性を確認するため小型のミキサセトラ抽出器を用いたフローシート実験を行った。その結果、共除染工程において U(VI) とともに抽出された Np の 99.98% を *n*-ブチルアルデヒドを用いた Np 分離工程において U から還元分離することができた。また、*iso*-ブチルアルデヒドを用いた U/Pu 分配工程では、99% 以上の Pu を U から還元分離することができた。

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1. INTRODUCTION

The control of ^{237}Np (an alpha emitter with a half-life: 2.14×10^6 y) in the reprocessing plant is required to avoid diffusion of the nuclide in the environment¹⁾.

After dissolved in HNO_3 solution, Np tends to diffuse in the Purex process due to the extractable Np(IV) and Np(VI) in the system of tri-n-butyl phosphate (TBP) diluted with saturated hydrocarbon diluent (e.g. n-dodecane (nDD)) and HNO_3 ²⁾ as shown in Fig. 1. Inextractable Np(V) is said to be stable in the dissolver solution of concentrated HNO_2 ($>10^{-3}$ M (mol/l)). Most of Np(V) is oxidized to Np(VI) by nitrous ion in the co-decontamination step and is extracted to the organic solvent together with U(VI) and Pu(IV). Koch reported that the addition of V(V) to the co-decontamination step was an effective technique to oxidize Np(V) to Np(VI) and to extract Np with high efficiency in the step³⁾. In the U/Pu partition step, Np(VI) is reduced to Np(IV) or Np(V) by reductants such as NH_2OH and U(IV) for Pu(IV). Thus, Np is distributed to both the U and the Pu purification cycles. Stripping the Np from the solvent before the U/Pu partition step is considered to be favorable in order to avoid diffusion of the Np into the down streams.

A process to separate Np before the U/Pu partition step has been studied by the authors using salt-free reagents which can be decomposed to gases and water. Neptunium should be selectively reduced from Np(VI) to Np(V) in the presence of U(VI) and Pu(IV). Kolarik proposed butyraldehyde as a selective Np(VI) reductant⁴⁾. Butyraldehyde is an organic compound of low molecular weight of 72.1 having a hydrophilic group(-CHO) and is distributed to both the 30 % TBP/nDD and HNO_3 solutions. The chemical formula, however, is not described in the report in spite of two isomers of butyraldehydes, n- and iso-butyraldehydes, as shown in Table 1. Based on the structural isomers, a difference in their reduction power between them is expected. In practice, redox potentials of n- and iso-butyraldehydes in 3 M HNO_3 at 298 °K were about 0.72 and 0.66 V vs. SCE, respectively. The potential of n-butyraldehyde is much higher than 0.09 V vs. SCE of the standard redox potential of U(VI)/U(IV) system, a little higher than 0.68 V vs. SCE of Pu(IV)/Pu(III) system and lower than 0.91 V vs. SCE of Np(VI)/Np(V) system⁵⁾. The potential of iso-butyraldehyde is a little lower than that of

Pu(IV)/Pu(III). Based on these findings, a kinetics study and a flow sheet study were conducted to develop the selective separation process of Np, Pu and U using n- and iso-butyraldehydes before the U/Pu partition step. Some of the results have been already reported⁶⁾.

The present report deals with the more detail study. In the kinetics study, the distribution ratios of n- and iso-butyraldehydes between the TBP/nDD and HNO₃ solutions and the reduction rates of Np(VI), Pu(IV) and U(VI) by the butyraldehydes are measured. In the flow sheet study, a new selective separation process of Np, Pu and U using n- and iso-butyraldehydes in the reprocessing is proposed and demonstrated using miniature mixer-settlers.

2. KINETICS STUDY ON Np, Pu AND U REDUCTION

2.1 Experimental

The distribution ratios (D) of n- and iso-butyraldehydes were measured by a batch-wise extraction method in the system of TBP/nDD and 3 M HNO₃ at 298 °K. The D was defined as the concentration ratio of butyraldehyde in organic phase to that in aqueous phase as follows:

$$D = \frac{[C_3H_7CHO \cdot nTBP]_{org.}}{[C_3H_7CHO]_{aq.}} \quad \text{-----(1)}$$

The concentration of TBP in the organic phase ranged from 0.0 to 2.0 M. The concentration of butyraldehyde in the HNO₃ solution was 0.06 M before adding the TBP/nDD solution. Mixing and settling times were 3.0 and over 10 min, respectively.

The concentration profiles of n- and iso-butyraldehydes in a miniature mixer-settler of 8 stages were obtained under the conditions of 1.7 M of n- or iso-butyraldehyde in the 30 % TBP/nDD and 3 M HNO₃ of scrub solution. The solvent and scrub solutions were fed at stage 1 and 8, respectively. The ratio of flow rate of solvent to that of scrub solution (O/A) was 5.

The scrubbing of 1 M n-butyraldehyde in the 30 % TBP/nDD with 3 M HNO₃, water and 0.5 M Na₂CO₃ was carried out in batch-wise experiments. The concentration

Pu(IV)/Pu(III). Based on these findings, a kinetics study and a flow sheet study were conducted to develop the selective separation process of Np, Pu and U using n- and iso-butyraldehydes before the U/Pu partition step. Some of the results have been already reported⁶⁾.

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of n-butyraldehyde was measured by a liquid chromatography after mixing with scrub solutions. The concentration of n-butyraldehyde was determined at the absorption peak of 210 nm.

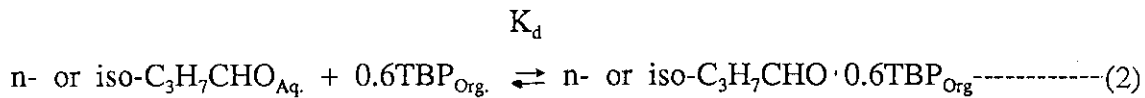
NpO_2 and PuO_2 were individually dissolved in 3 M HNO_3 by heating with an infrared lamp. Uranium nitrate solution was obtained by dissolving the uranyl nitrate powder ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) in 3 M HNO_3 . The Np valency was initially adjusted to Np(VI) by using an electrolytic cell with Pt electrodes. The HNO_3 solution containing Np(VI), Pu(IV) or U(VI) was put into a stirred optical cell (light path: 1 cm) of absorption spectrophotometer as shown in Fig. 2. The reaction was started by adding one of the butyraldehyde reductants into the cell. The concentration change of reaction products were detected at the absorption peaks of 983 nm for Np(V), 603 nm for Pu(III) and 648 nm for U(IV). The experiments were carried out under HNO_3 of 0.75 - 6.0 M and temperature of 283 - 323 °K in the presence of the reductants of more than 10-fold amount stoichiometrically required. The reduction rate of Np(VI) in the solvent of 30 % TBP/nDD was measured in the same way.

Commercial reagents of n- and iso-butyraldehydes, TBP and nDD were used without any special pretreatments. Uranium and HNO_3 were analyzed by an alkalimetric titration method. An alpha-ray counter and a spectrophotometer were used to analyze the concentrations and valency state of Np, Pu and U. The concentration of HNO_2 was measured by a spectrophotometric method using chromogenic reagents⁷⁾.

2.2 Results and discussion

2.2.1 Distribution behavior of n- and iso-butyraldehydes

Figure 3 shows the distribution ratios (D) of n- and iso-butyraldehydes as a function of TBP concentration in organic phase in the system of TBP/nDD and 3 M HNO_3 at 298 °K in log-log plot. Both values of the distribution ratio are almost the same. The values of log D of both butyraldehydes were about 0.3 at log $[\text{TBP}]_{\text{org}}$ of 0, that is, the distribution ratios of butyraldehydes in the system of 30 % (1.1 M) TBP/nDD and 3 M HNO_3 were about 2. The slope of straight line given in the figure is 0.6. These data are in favor of the following extraction formula:



where the equilibrium constant (K_d) was about 2 from the following equation:

$$K_d = \frac{[\text{C}_3\text{H}_7\text{CHO} \cdot n\text{TBP}]_{\text{org.}}}{[\text{C}_3\text{H}_7\text{CHO}]_{\text{aq.}} \cdot [\text{TBP}]_{\text{org.}}^n} \text{-----} (3)$$

The distribution behaviors of n- and iso-butyraldehydes in the mixer-settler were investigated. Figure 4 shows the concentration profiles in both organic and aqueous phases in the mixer-settler with the distribution ratio of n-butyraldehyde at each stage. Initial concentration of n-butyraldehyde in the organic feed was 1.7 M. The concentration of n-butyraldehyde in the organic phase at stage 8 was 1.3 M. This means that about 76 % of total n-butyraldehyde was left with the TBP. Also the figure shows that the distribution ratio of n-butyraldehyde was not about 2 but 4.2. The larger value was obtained than that in the batch-wise experiment. From the concentration profiles and feed rates of both phases, it was found that about 20 % of the total butyraldehyde was lost. These findings may show that n-butyraldehyde was decomposed mainly in the aqueous phase during the mixer-settler experiment. The concentration profile of iso-butyraldehyde was nearly the same as that of n-butyraldehyde under the same conditions.

The preliminary experiment on batch-wise scrubbing of n-butyraldehyde in the 30 % TBP/nDD with 3 M HNO_3 , water and 0.5 M Na_2CO_3 was carried out in order to find the distribution behavior of n-butyraldehyde in the U stripping and the solvent washing steps. Figure 5 shows the concentration of n-butyraldehyde in the organic phase as a function of number of batch-wise scrubbing. The concentration of n-butyraldehyde decreases almost linearly with number of scrubbing. This means that 10 - 40 % of n-butyraldehyde in the solvent was scrubbed in each scrubbing and that the scrubbing efficiency of n-butyraldehyde in the organic phase with both water and 0.5 M Na_2CO_3 was nearly the same as that with 3 M HNO_3 .

These results show that most of n- and iso-butyraldehydes fed to the co-decontamination step or the Pu/U partition step will be left with the TBP solvent and some of them will be back-extracted to the aqueous phase in the U purification and the solvent washing steps. The diffusion of butyraldehyde into other extraction steps should

be prevented in order to avoid reduction reactions of Np, Pu and U. Thus, the decomposition of butyraldehyde in organic and aqueous solutions is required.

The decomposition experiments of n- and iso-butyraldehyde in organic and aqueous phases were carried out by an air oxidation method. The decomposition behavior of n-butyraldehyde in 3 M HNO₃ and 30 % TBP/nDD phases at 333 and 293 °K is shown in Figs. 6 and 7, respectively. In the latter case, 3 M HNO₃ was added to decompose n-butyraldehyde in the aqueous phase during back-extraction of n-butyraldehyde from the organic phase. In both phases the decomposition rate of n-butyraldehyde at 333 °K is larger than that at 293 °K. More than 99 % of n-butyraldehyde in both phases was decomposed within 15 min at 333 °K. The decomposition behavior of iso-butyraldehyde was nearly the same as that of n-butyraldehyde.

These results show that n- and iso-butyraldehydes dissolved in organic and aqueous solutions can be easily decomposed by an air oxidation method.

2.2.2 Reduction behavior of Np, Pu and U in HNO₃

The reduction behavior of Np(VI), Pu(IV) and U(VI) by n- and iso-butyraldehydes in 3 M HNO₃ are shown in Fig. 8. In the case of n-butyraldehyde, only Np(VI) was reduced to Np(V). In the case of iso-butyraldehyde, U(VI) was not reduced and, however, not only Np(VI) but also Pu(IV) was reduced. The reduction product of Np(V) was further reduced up to Np(IV) gradually by iso-butyraldehyde as shown in Fig. 9 where the time dependence of absorbances of Np(IV), Np(V) and Np(VI) is shown with the rest potential in the solution. The figure shows that the rest potential dropped rapidly after the addition of iso-butyraldehyde and then rose slowly. At the time of about 1,200 min the rest potential rose quickly and Np(V) was oxidized to Np(VI) at nearly the same time. This reoxidation of Np(V) seems to be due to the disappearance of iso-butyraldehyde. The reduction and oxidation of Np seems to correspond to the rest potential approximately. The reduction rates of Np(VI) and Pu(IV) were accelerated with the increase of acidity, butyraldehyde concentration and temperature in solutions.

The order of strength of the reduction power of the butyraldehydes for Np(VI), Pu(IV) and U(VI) is in the reverse of that of the redox potential of the butyraldehydes. These data show that n-butyraldehyde is a weaker and more favorable reductant than iso-

butyraldehyde for the selective reduction of Np(VI) to Np(V) in the system of U(VI)-Np(VI)-Pu(IV)-HNO₃. Iso-butyraldehyde having much higher Np(VI) reduction rate than n-butyraldehyde is favorable as a reductant for Np(VI) in the system of U(VI)-Np(VI)-HNO₃ without Pu(IV). Iso-butyraldehyde having the reduction power of Pu(IV) is considered to be applicable as a reductant of Pu(IV) in the U/Pu partition step.

In the standard U/Pu partition step, a decomposing reagent of HNO₂ such as N₂H₄ is required in order to prevent reoxidation of Pu(III). The decomposition rates of HNO₂ by n- and iso-butyraldehyde were measured in HNO₃ solutions. Figure 10 shows the decomposed fraction of HNO₂ by 0.06 M n- and iso-butyraldehyde in 3 M HNO₃ at 293 °K as a function of time. In both cases of n- and iso-butyraldehyde, 1 x 10⁻³ M HNO₂ in the HNO₃ solution was decomposed within 15 min. These findings indicate that iso-butyraldehyde as the Pu(IV) reductant has a possibility of improving the U/Pu partition process without the addition of any decomposing reagent of HNO₂.

2.2.3 Reduction behavior of Np and Pu in 30% TBP/n-dodecane solution

The reduction of Np(VI) and Pu(IV) by n- and iso-butyraldehydes is expected to occur in not only aqueous phase but also organic phase since the butyraldehydes are distributed to the both phases. The reduction rate of Np(VI) by iso-butyraldehyde in 30% TBP/nDD solution was studied. The reduction behavior of Np(VI) by iso-butyraldehyde in the solution saturated with HNO₃ is shown in Fig. 11, compared with that in 3 M HNO₃ solution. The concentration ratio of iso-butyraldehyde to Np(VI) was about 70 in each solution. In the aqueous solution, the Np(VI) reduction was finished completely within 3 min. On the other hand, the Np(VI) reduction in the organic solution was slowly proceeded. The reduced fraction of Np(VI) was less than 15 % even at the reaction time of 17 min. This result agrees with that the reduction rate of Np(VI) by U(IV) in TBP solutions was much smaller than that in HNO₃ solution⁸⁾. The difference in the reduction rate between aqueous and organic solutions is considered to be mainly due to the difference of activity coefficients of Np(VI), iso-butyraldehyde and HNO₃⁸⁾. By the same reason, it is similarly considered that the reduction rate of Pu(IV) by iso-butyraldehyde in the organic solution is smaller than that in the aqueous solution. The reduction rate of Np(VI) by n-butyraldehyde in aqueous solution is much smaller than that by iso-butyraldehyde under the same conditions. Thus, it is guessed that the

reduction rate of Np(VI) by n-butyraldehyde in the organic solution is much smaller than that by iso-butyraldehyde. These data show that the reduction of Np(VI) and Pu(IV) by the butyraldehydes occurs mainly in the aqueous solution, although the butyraldehydes are distributed to the organic solution rather than to aqueous solution.

3. FLOW SHEET STUDY ON THE Np, Pu AND U SEPARATION PROCESS

3.1 Application of n- and iso-butyraldehydes to the Purex process

Based on the difference in selectivity and reduction power between n- and iso-butyraldehydes, three applications of the butyraldehydes for the selective separation of Np, Pu and U in the Purex process can be considered as shown in Fig. 12. In the Np separation step, only Np can be separated from Pu and U with n-butyraldehyde. In the U/Pu partition step, Pu can be separated from U with iso-butyraldehyde. In the U purification step, n- and iso-butyraldehydes can be used to separate the remaining Np and Pu from U. However, iso-butyraldehyde is more favorable than n-butyraldehyde because the reduction rates of Np and Pu by the former are higher than those by the latter.

By combining the initial two applications, a new separation process can be proposed as shown in Fig. 13. In the process, n-butyraldehyde is used for Np(VI) reduction in the Np separation step and iso-butyraldehyde is used for Pu(IV) reduction in the U/Pu partition step.

In this flow sheet study, the performance of the new process was demonstrated by using mixer-settlers.

3.2 Experimental

Three runs were carried out to measure the separation efficiency of Np, U and Pu in the separation process. In the first run (Run A), three miniature mixer-settlers were used to demonstrate the effectiveness of the process in the system of Np, Pu and U. In the second and third runs (Run B and C), conditions of the flow sheet were modified

reduction rate of Np(VI) by n-butyraldehyde in the organic solution is much smaller than that by iso-butyraldehyde. These data show that the reduction of Np(VI) and Pu(IV) by the butyraldehydes occurs mainly in the aqueous solution, although the butyraldehydes are distributed to the organic solution rather than to aqueous solution.

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to increase the Np extraction efficiency in the co-decontamination step and the Np separation efficiency in the Np separation step in the system of Np and U. The main difference between Run B and C is the flow rate of scrub solution. The experiments were carried out at room temperature. In each run, organic solvent was fed for more than 3-fold residence time in the mixer-settlers in order to obtain the concentration profiles of Np, Pu and U at a steady state.

In Run A, three miniature mixer-settlers were used in a glove box as shown in Photo. 1. The experimental flow sheet shown in Fig. 14 consisted of 5 steps; co-decontamination, Np separation, U·Pu recovery, U/Pu partition and U stripping steps. Each miniature mixer-settler had 16 stages. Each volume of the mixer and the settler was 6 ml and 17 ml, respectively. The simulated feed solution containing 250 g/l of U, 1.85 g/l of Pu, 0.53 g/l of $^{237}\text{Np} + ^{239}\text{Np}$ and 3.0 M HNO_3 was fed at stage 16 of the mixer-settler for the co-decontamination step. The valency states of U, Pu and Np in the solution were adjusted to Np(VI), Pu(IV) and U(VI), respectively, by an electrolytic oxidation technique. The cathodic potential was +1.50 V vs. SCE. After the end of electrolytic oxidation, the rest potential in the solution dropped rapidly to +1.10 V vs. SCE and then slowly to 0.851 V vs. SCE. A spectrophotometric analysis before the experiment showed that Np, Pu and U in the solution were adjusted almost completely to Np(VI), Pu(IV) and U(VI), respectively. However, Np valency changed during the experiment. After 5 h of the experiment, about 90 % of Np remained in hexavalent state and the rest was in pentavalent state. The ratio of flow rate of organic solution to that of aqueous solution (O/A) in each step is also shown in Fig. 14.

In Run B using a miniature mixer-settler of 16 stages, NH_4VO_3 was used as an oxidant of Np(V) to Np(VI) in order to extract Np effectively in the co-decontamination step. And each flow rate of feed and solvent, reductant and scrub solutions was reduced one-half of that in Run A. The residence time of each solution in the Np separation step was doubled. The flow sheet shown in Fig. 15 consisted of three steps: the Np oxidation step of 4 stages, the co-decontamination step of 4 stages and the Np separation step of 8 stages. The Np valency of the feed solution of 3 M HNO_3 containing 180 g/l of U and 0.0675 g/l of $^{237}\text{Np} + ^{239}\text{Np}$ was not adjusted. About 30 % of the Np in the solution containing of 3×10^{-3} M HNO_2 was in hexavalent state and the rest was in pentavalent state. Ammonium vanadate of 0.5 g/l in 3 M HNO_3 was fed at stage 4.

In Run C, the flow rate of the Np scrub solution was increased from 20 to 30 ml/min. The flow ratio (O/A) in the Np separation step was decreased from 5.7 to 3.8. As shown in Fig. 16, the other experimental conditions are nearly the same as those in Run B.

3.3 Results and discussion

3.3.1 Separation of Np, Pu and U (Run A)

In Run A, the concentrations of Np, Pu and U in each step of the flow sheet and the fractions of Np, Pu and U distributed to the products and raffinate are shown in the Fig. 14 and Table 2, respectively. In the co-decontamination step, more than 99.9 % of total U and total Pu and 90 % of total Np were extracted by the solvent. Ten percent of total Np flowed to the raffinate. Some of the Np in the feed initially adjusted in hexavalent state changed during the experiment. At the end of the experiment, about 90 % of Np was in hexavalent and the rest of Np was in pentavalent state. These results show that Pu(IV) and U(VI) were stable and that Np(VI) was not stable in 3 M HNO₃. Np(VI) seems to be reduced by HNO₂ generated by the reduction reaction of HNO₃ in the solution. The valency of Np in the raffinate was pentavalent. The fraction of Np flowed to the raffinate was nearly consistent with the fraction of Np(V) in the feed solution at the end of the experiment. The concentration of HNO₂ in the raffinate was 1×10^{-5} M. These data show that Np(VI) in the feed was extracted in the co-decontamination step of 16 stages and that, however, Np(V) was stable and not oxidized in such relatively low concentration of HNO₂ in the step. This result indicates that the valency adjustment of Np in the feed solution and/or in the co-decontamination step is effective to extract Np with higher efficiency in the real co-decontamination step.

In the Np separation step of 13 stages of the second mixer-settler, about 91 % of the Np was separated as Np product from the solvent stream loaded with Np, Pu and U. About 82 % of the total Np fed to the first mixer-settler was recovered in the Np product. This means that Np(VI) was selectively reduced to Np(V) by n-butyraldehyde in the step.

In the U/Pu partition step of 10 stages, more than 99 % of the Pu entered to the third mixer-settler was effectively separated from U in the organic phase. About 99.2 %

of the total Pu was recovered in the Pu product. This means that Pu(IV) was effectively reduced by iso-butyraldehyde without decomposing reagents of HNO_2 .

3.3.2 Separation of Np and U under the condition of high O/A (Run B)

In Run B, the concentrations of Np and U in each step of the flow sheet and the fractions of Np and U distributed to the products and raffinate are shown in the Fig. 15 and Table 2, respectively. The concentration profile of Np in both organic and aqueous phases in the flow sheet is shown in Fig. 17. In the co-decontamination step, more than 99.9 % of total U fed to the step was extracted by the solvent. As for Np, 99.85 % of total Np fed to the step was extracted by the solvent together with U and flowed to the Np separation step. The Np concentration in the aqueous phase decreases gradually along with stages in the co-decontamination step. The ratio of Np concentration at stage 5 to that in feed solution was about 0.7. This means that about 70 % of the Np fed to the step flowed to the Np oxidation step and the rest of the Np was extracted by the solvent. The fraction of extracted Np in the co-decontamination step was nearly the same as the fraction of Np(VI) in the feed solution. These results show that the fraction of extracted Np in the real co-decontamination step without addition of any redox reagents depends strongly on the fraction of Np(VI) in the feed solution.

In the Np oxidation step of 4 stages, Np concentration in aqueous phase decreases constantly along with stages by the about three-fourth per stage. The valency of Np in the aqueous phase at stage 5 was almost pentavalent and that at stage 1 was almost hexavalent. This indicates that Np(V) in aqueous phase was oxidized to Np(VI) by NH_4VO_3 effectively and extracted by the solvent in the step. Based on the results, if the Np oxidation step using an oxidant such as V(V) is set at the raffinate side of the co-decontamination step, the valency adjustment of Np in the feed solution might be not required in order to extract Np effectively in the real co-decontamination step.

In the Np separation step of 8 stages, Np concentrations in both organic and aqueous phases decrease with nearly the same slope along with stages. In the step, about 99.3 % of the total Np fed to the co-decontamination step was back-extracted as Np product from the solvent stream loaded with Np and U.

3.3.3 Separation of Np and U under the condition of low O/A (Run C)

In Run C, the concentrations of Np and U in each step of the flow sheet and the fractions of Np and U distributed to the products and raffinate are shown in the Fig. 16 and Table 2, respectively. In the co-decontamination step, 99.2 % of the total Np fed to the step was extracted with U. In the Np separation step of 8 stages, more than 99.98 % of Np extracted with U(VI) was back-extracted from the solvent. The Np separation efficiency in the Np separation step was increased by decreasing the O/A ratio from 5.7 to 3.8.

These results indicate that the process conditions of the residence time of both phases and the O/A ratio improve the Np separation efficiency.

3.3.4 Decontamination factors of Np and Pu from U

These experimental data were compared with the data designed in the Thermal Oxide Reprocessing Plant (THORP)⁹⁾ in order to evaluate the separation efficiency of Np, Pu and U in the new separation process. In the THORP plant, the total decontamination factors designed for Np and Pu are reported to be 314 and 7.65×10^5 , respectively⁹⁾. In Run A, the Np decontamination factor to the U stream obtained in the Np separation step was 11.1 and the total Np decontamination factor to the U stream obtained was 108. In Run B, the Np decontamination factor to the U stream obtained in the Np separation step was 136. In Run C, more than 5,000, much higher than that designed in the THORP plant, was obtained in the Np separation step.

As for Pu, about 9×10^4 of decontamination factor to the U stream was obtained in Run A. The decontamination factor is smaller by one order magnitude than the designed value in the THORP plant. If it is required to meet the designed value for Pu, optimization of the process conditions, such as concentrations of iso-butyraldehyde and HNO_3 , temperature and residence time in the U/Pu partition step, is needed. Plutonium decontamination in the U purification step may be required furthermore.

These results suggest that it is possible to separate Np, Pu and U sufficiently by n- and iso-butyraldehydes in the modified Purex process. Further optimization of the process conditions will increase the separation efficiency.

4. CONCLUSIONS

A kinetics study and a flow sheet study were conducted to develop a new selective separation process of Np, Pu and U by using n- and iso-butyraldehydes in the reprocessing. The experimental results are summarized as follows:

(1) The distribution ratio of n-butyraldehyde in the TBP/nDD and HNO₃ system was nearly the same as that of iso-butyraldehyde. The Distribution ratios increased with TBP concentration in the organic phase. The equilibrium constant (K_d) in the obtained extraction formula was about 2.

(2) Normal- and iso-butyraldehydes were found to be favorable reductants for the selective Np(VI) reduction in the presence of U(VI) and/or Pu(IV). Normal- butyraldehyde has much higher selectivity and much lower reduction rate than iso- butyraldehyde. Thus, n-butyraldehyde can be used to reduce Np(VI) selectively and iso-butyraldehyde can be used to reduce not only Np(VI) but also Pu(IV). Consequently, a new selective separation process of Np, Pu and U by using n- and iso-butyraldehydes as reductants for Np(VI) and Pu(IV), respectively, was proposed.

(3) Flow sheet experiments using miniature mixer-settlers showed that 99.98 % of Np extracted by 30 % TBP/nDD solvent together with U(VI) in the co-decontamination step was reduced by n-butyraldehyde and separated from U in the Np separation step and that more than 99 % of Pu was reduced by iso-butyraldehyde and separated from U in the U/Pu partition step.

These data show that Np, Pu and U can be separated selectively in the modified Purex process using n- and iso-butyraldehydes.

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Table 1 Characteristics of n- and iso-butyraldehydes

COMPOUND	N-BUTYRALDEHYDE	ISO-BUTYRALDEHYDE
RATIONAL FORMULA	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=O}$	$\begin{array}{c} \text{CH}_3\text{-CH-CH=O} \\ \\ \text{CH}_3 \end{array}$
PRIMARY OXIDATION PRODUCT	N-BUTYLIC ACID	ISO-BUTYLIC ACID
FINAL OXIDATION PRODUCT	$\text{CO}_2 + \text{H}_2\text{O}$ (SALT-FREE REDUCTANT)	
CONCENTRATION OF BUTYRALDEHYDE SATURATED IN 3 M HNO_3 AT 298 °K	0.6 M	0.3 M

Table 2 Distribution behavior of Np, Pu, and U in the flow sheet experiments (Run A, B and C).

Run No.	RAFFINATE	Np PRODUCT	Pu PRODUCT	U PRODUCT	STRIPPED SOLVENT	
A	Np	10.00 %	81.9 %	7.1 %	1.0 %	0.00 %
	Pu	0.00 %	0.74 %	99.2 %	0.06 %	0.00 %
	U	0.00 %	0.02 %	2.40 %	97.6 %	0.00 %
B	Np	0.15 %	99.12 %	-	0.73 %	-
	U	0.00 %	2.2 %	-	97.8 %	-
C	Np	0.76 %	99.23 %	-	0.01 %	-
	U	0.00 %	2.4 %	-	97.6 %	-

EXTRACTABILITY BY TBP	
Np VALENCY	EXTRACTABILITY
Np(IV)	EXTRACTABLE
Np(V)	INEXTRACTABLE
Np(VI)	EXTRACTABLE

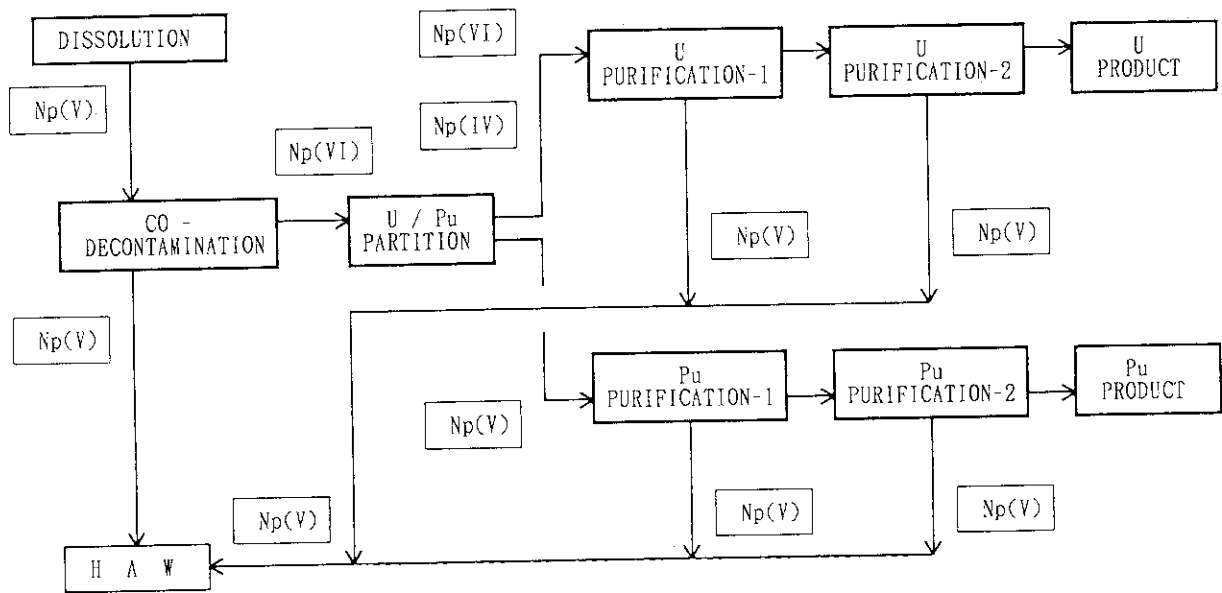


Fig. 1 Distribution behavior of Np in Purex process.

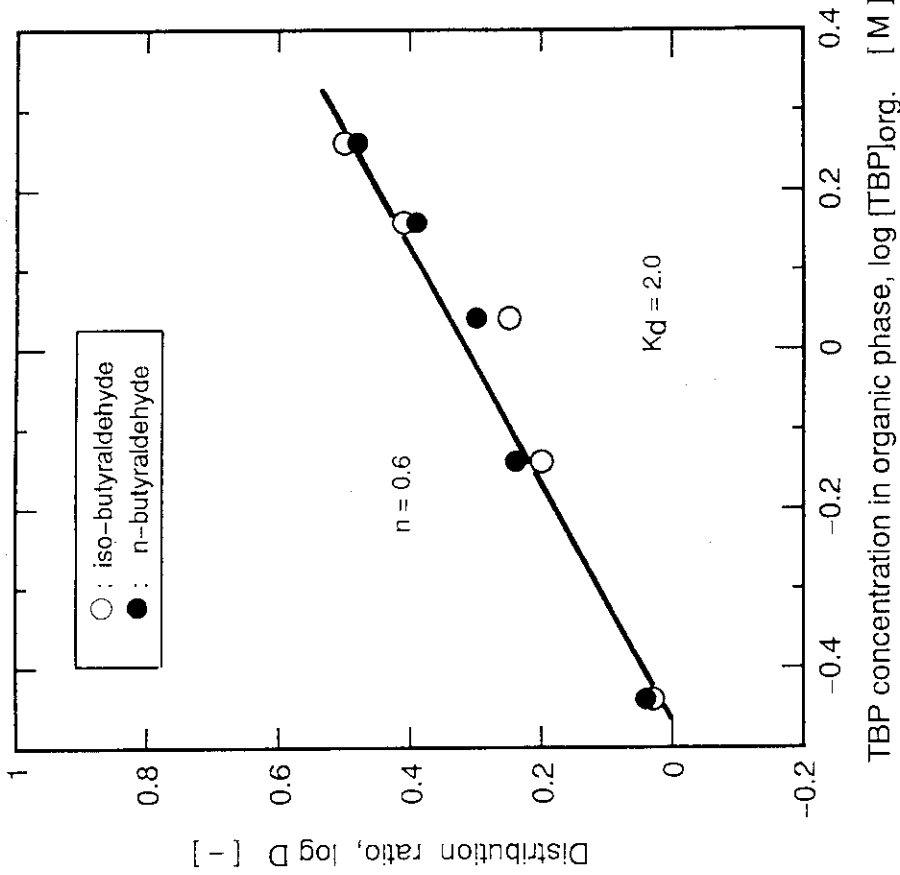


Fig. 3 Distribution ratios of n- and iso-butyraldehydes as a function of TBP concentration in organic phase in the system of TBP/nDD and 3 M HNO₃ at 298 °K.

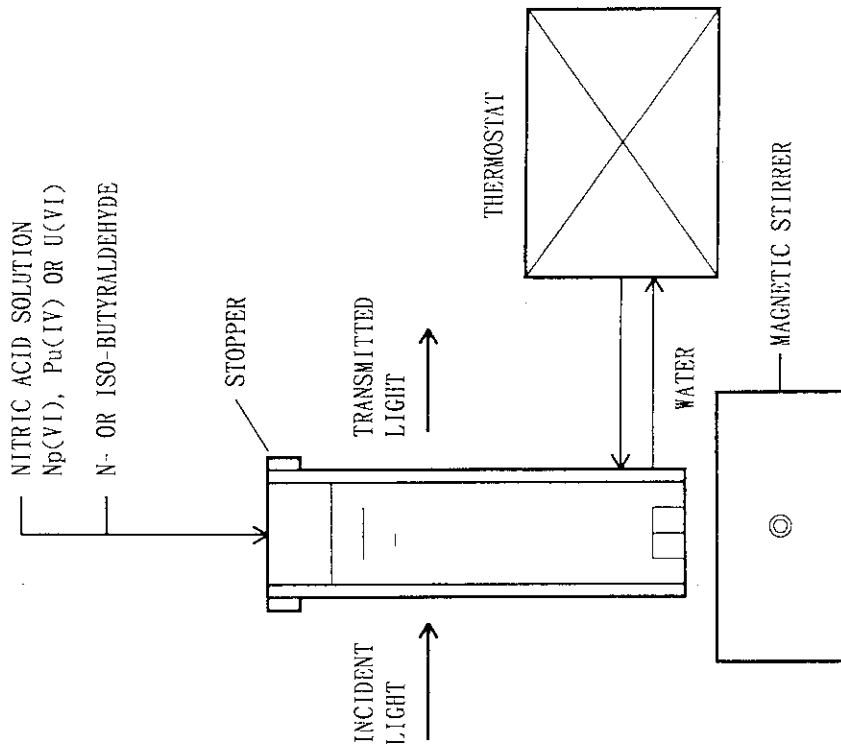


Fig. 2 Optical cell of absorption spectrophotometer.

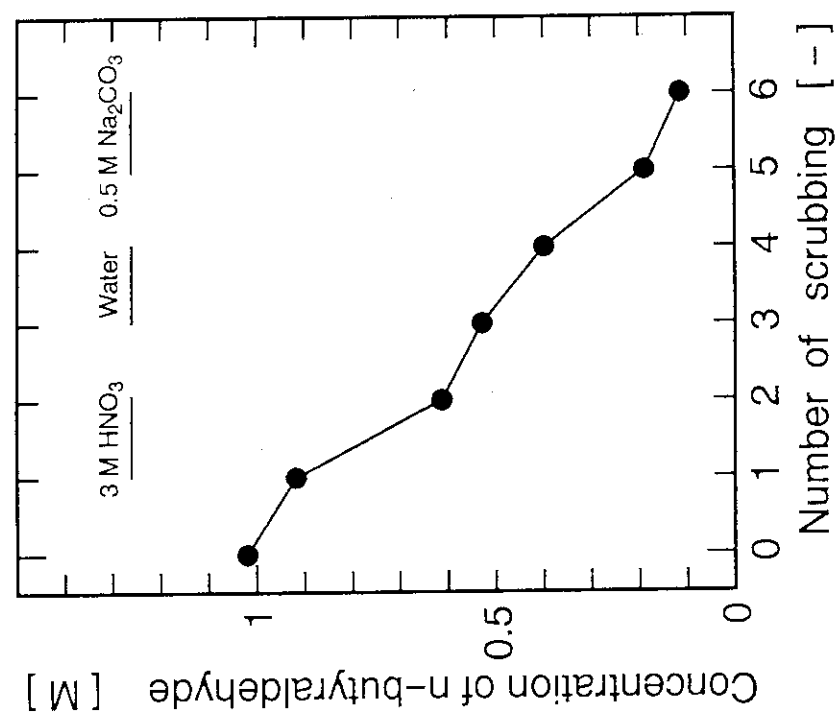


Fig. 5 Concentration of n-butyraldehyde in 30 % TBP/nDD as a function of number of batch-wise scrubbing with 3 M HNO₃, water and 0.5 M Na₂CO₃. Initial concentration of n-butyraldehyde: 1 M, O/A: 1.

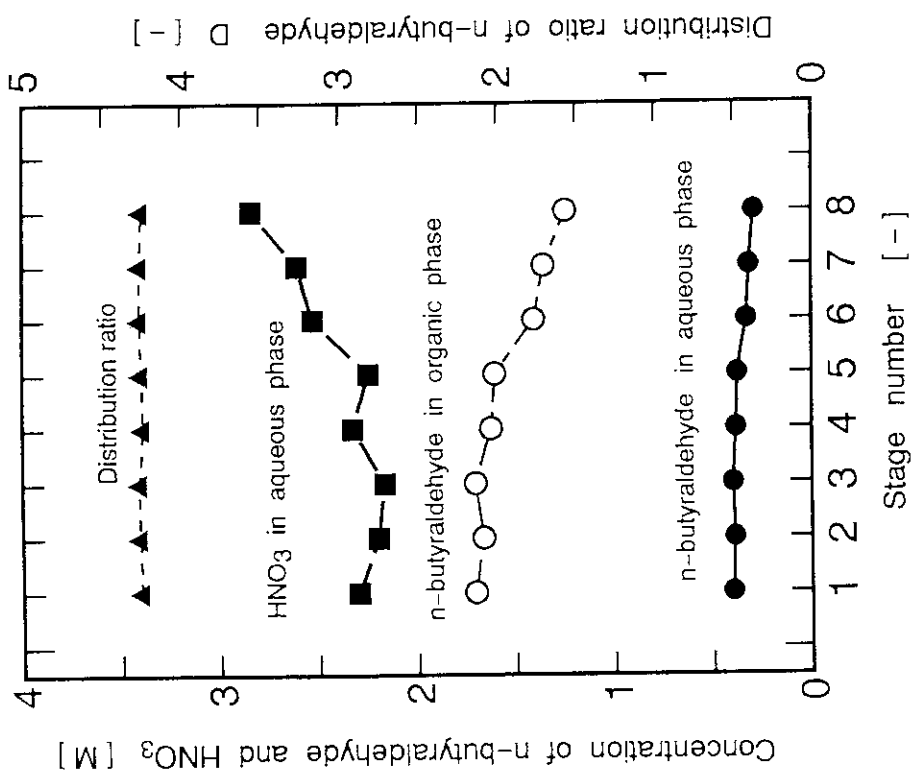


Fig. 4 Concentration profile of n-butyraldehyde in the mixer-settler. Initial concentration of n-butyraldehyde in organic phase: 1.71 M. Solvent flow rate: 200 ml/h, Scrub (3 M HNO₃) flow rate: 40 ml/h, O/A: 5.

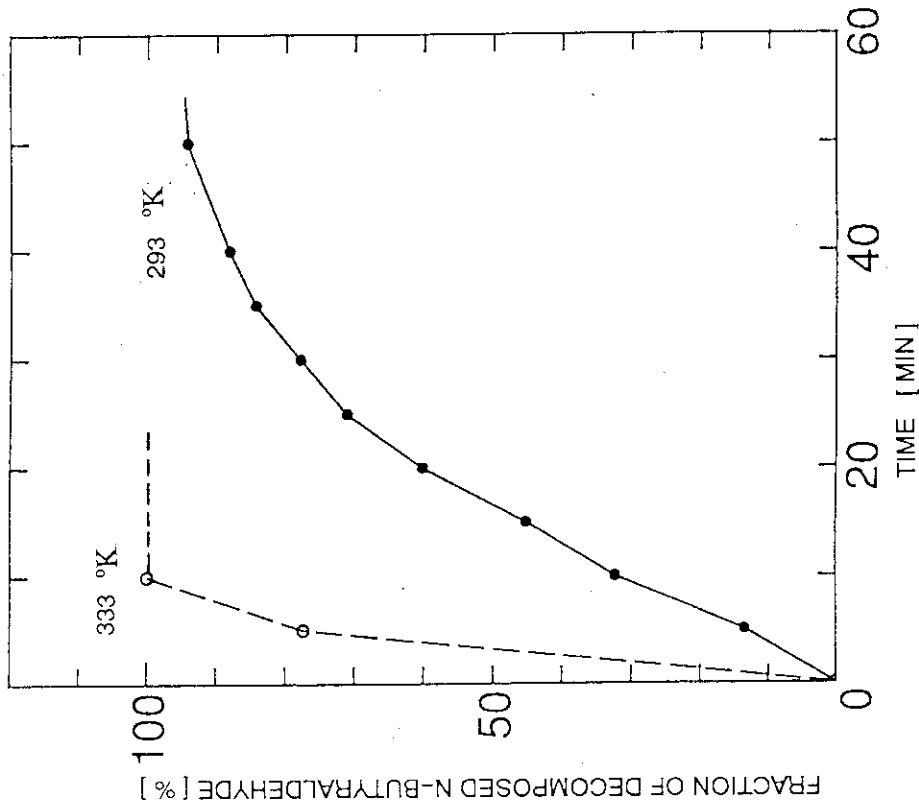


Fig. 7 Decomposition of n-butyraldehyde in 30 % TBP/nDD with back-extracting. Initial concentration of n-butyraldehyde: 0.1 M, Scrub solution: 3 M HNO₃, O/A: 1.

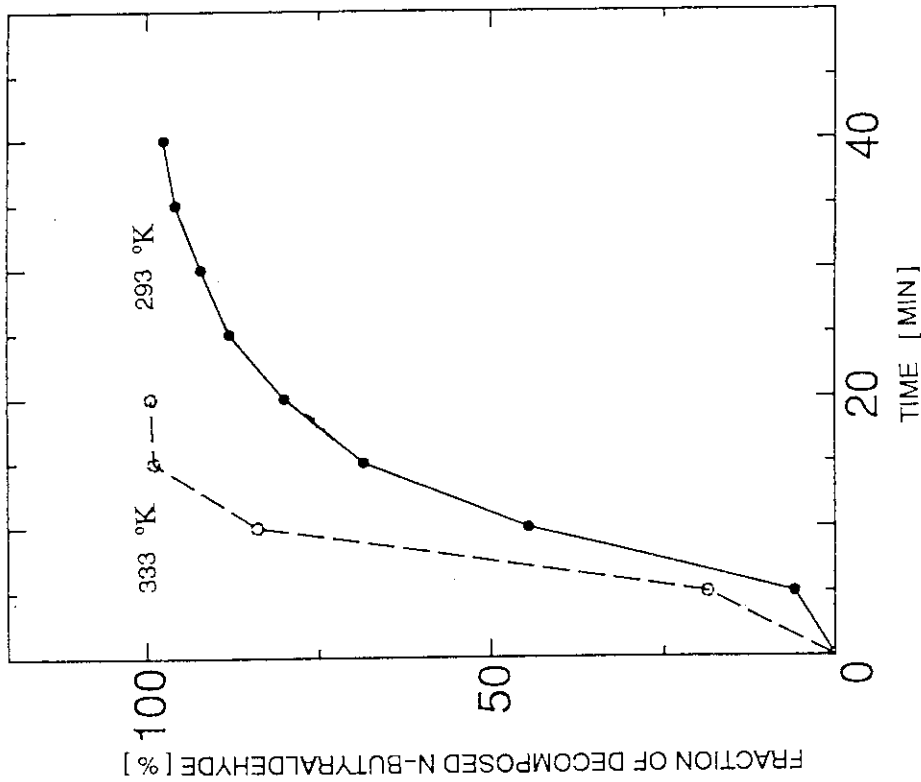


Fig. 6 Decomposition of n-butyraldehyde in 3 M HNO₃. Initial concentration of n-butyraldehyde: 0.1 M.

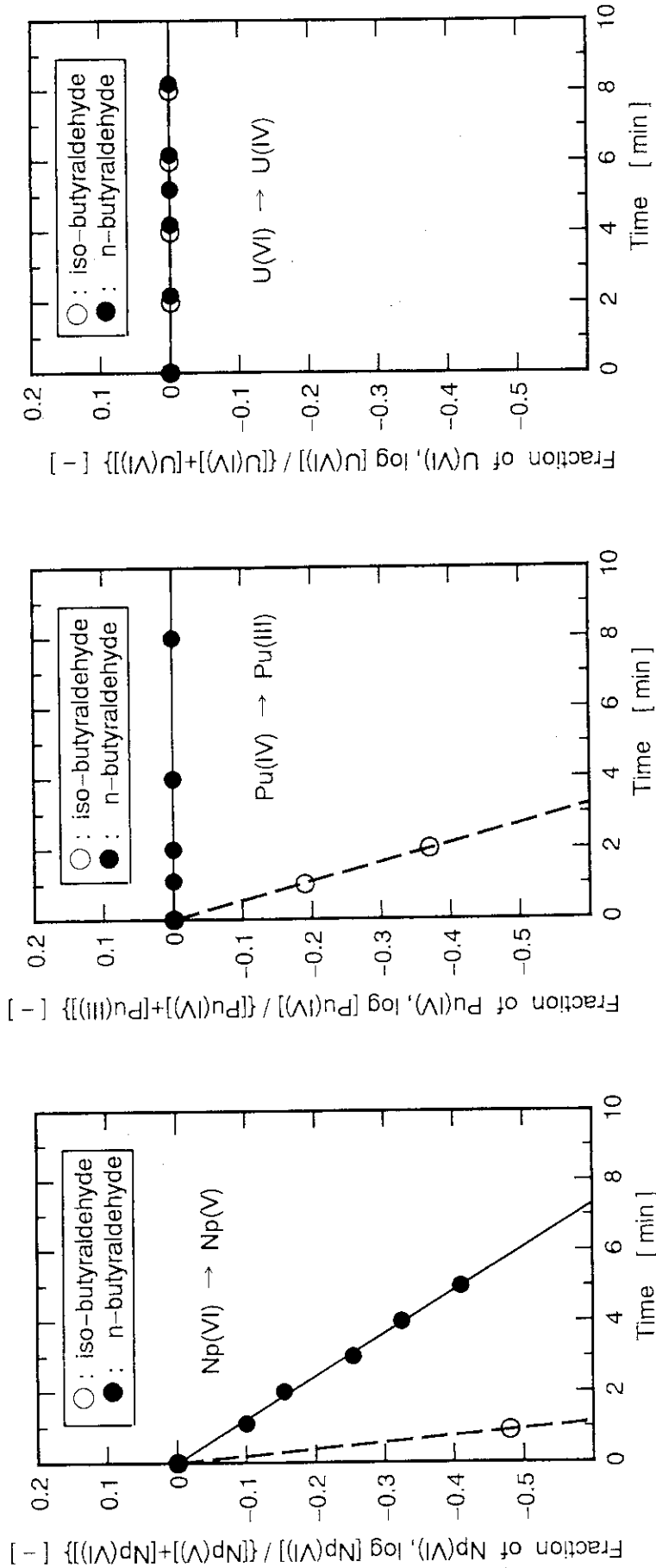


Fig. 8 Reduction of Np(VI), Pu(IV) and U(VI) with n- and iso-butyraldehydes. Np(VI): 0.13 g/l, Pu(IV): 5.5 g/l, U(VI): 20 g/l, H⁺: 3 M, Temp.: 293 °K.

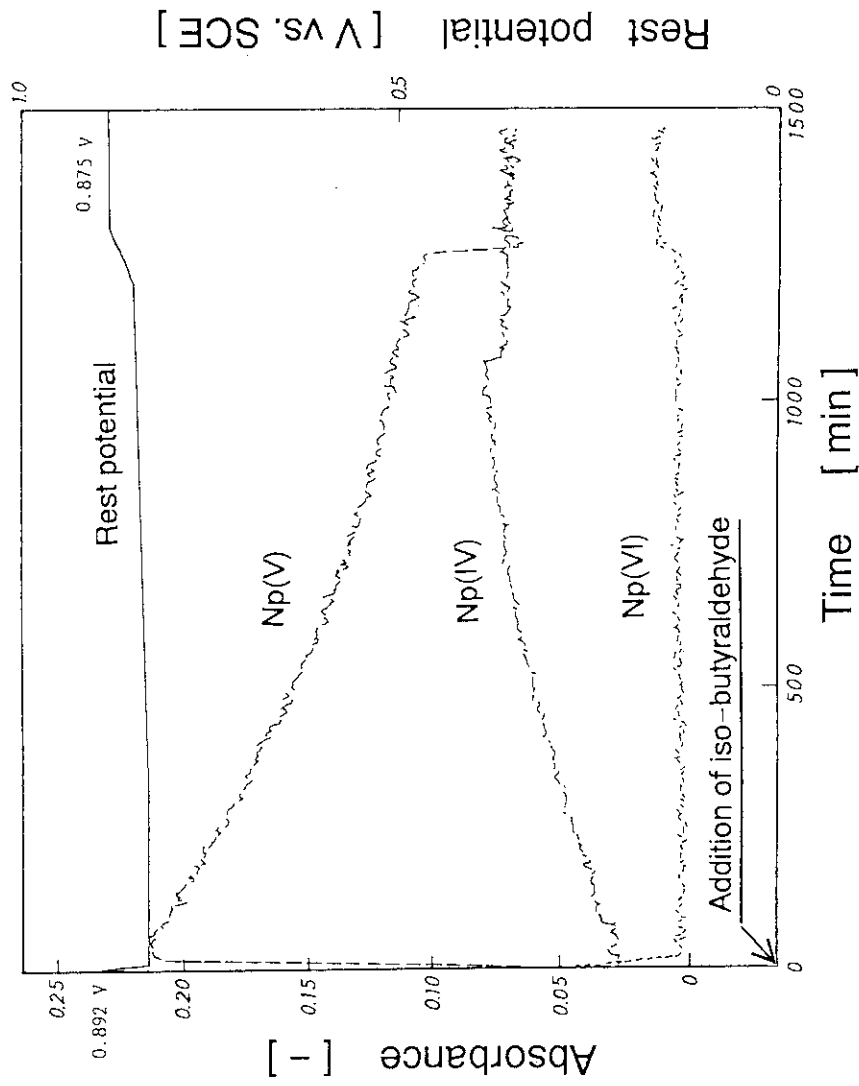


Fig. 9 Time dependence of absorbances of Np(IV), Np(V), Np(VI) and rest potential. Np(VI): 0.12 g/l, H^+ : 4.5 M, iso-butylaldehyde: 0.1 M, Temp.: 298 °K.

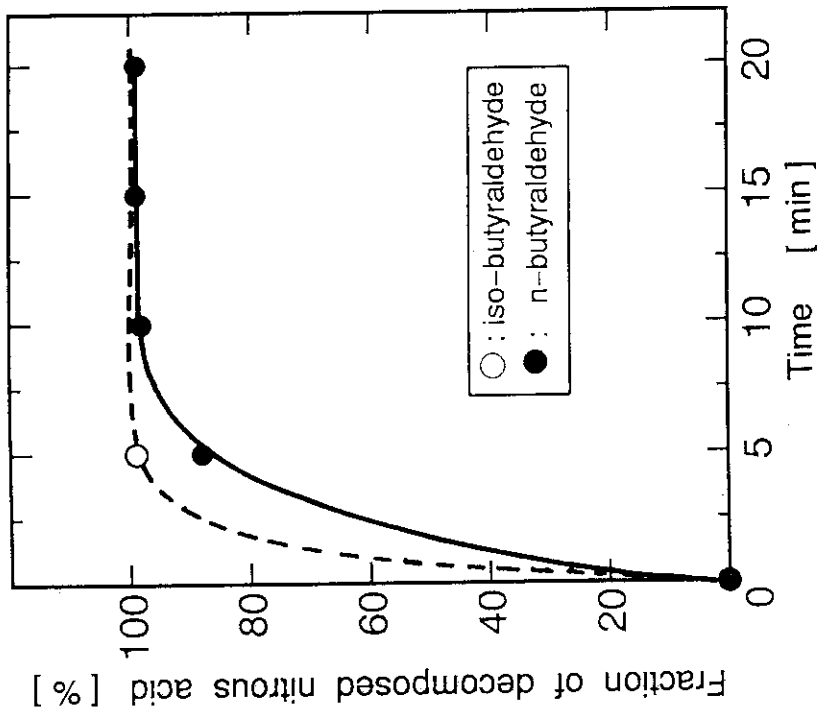


Fig. 10 Decomposition of HNO_2 with n- and iso-butylaldehydes in HNO_3 . HNO_2 : 0.001 M, HNO_3 : 3 M, n- and iso-butylaldehydes: 0.06 M.

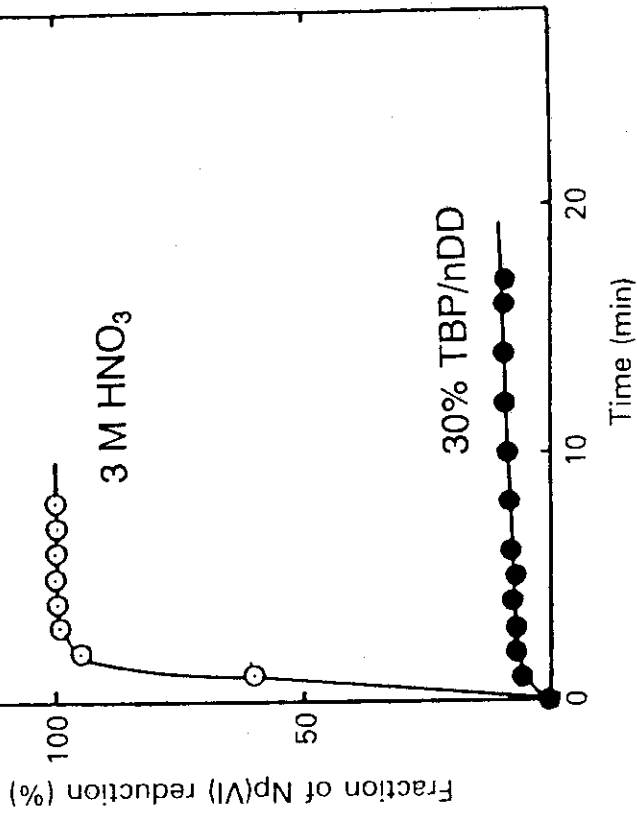
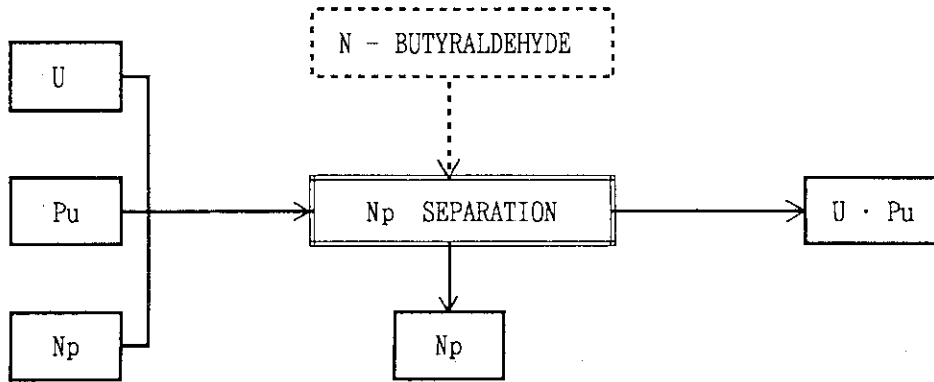
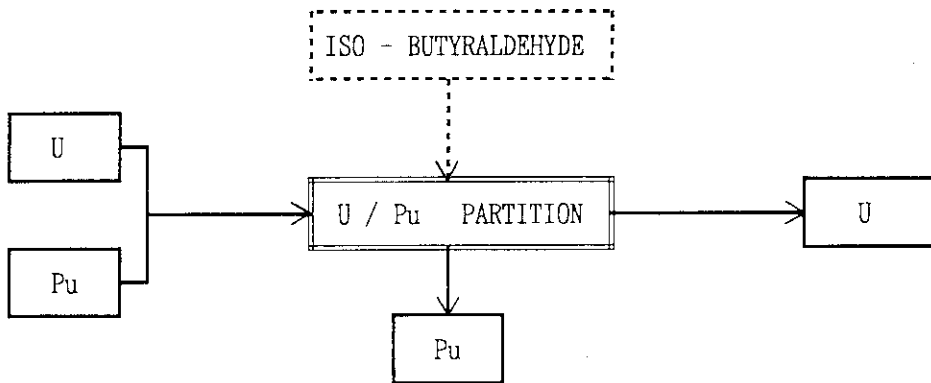


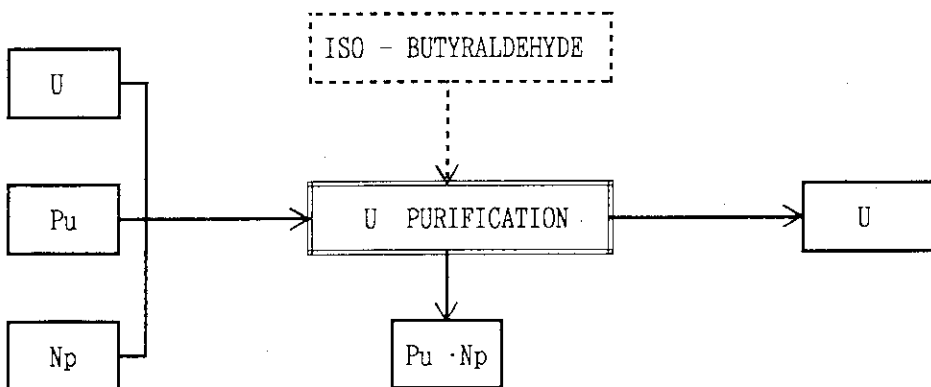
Fig. 11 Reduction of Np(VI) with iso-butylaldehyde in aqueous solution TBP/nDD solvent saturated with HNO_3 . Np(VI) : 0.20 g/l, iso-butylaldehyde: 0.06 M, Temp.: 298 °K.



① Np SEPARATION STEP



② U / Pu PARTITION STEP



③ U PURIFICATION STEP

Fig. 12 Use of n- and iso-butyraldehydes for Np/Pu/U separation.

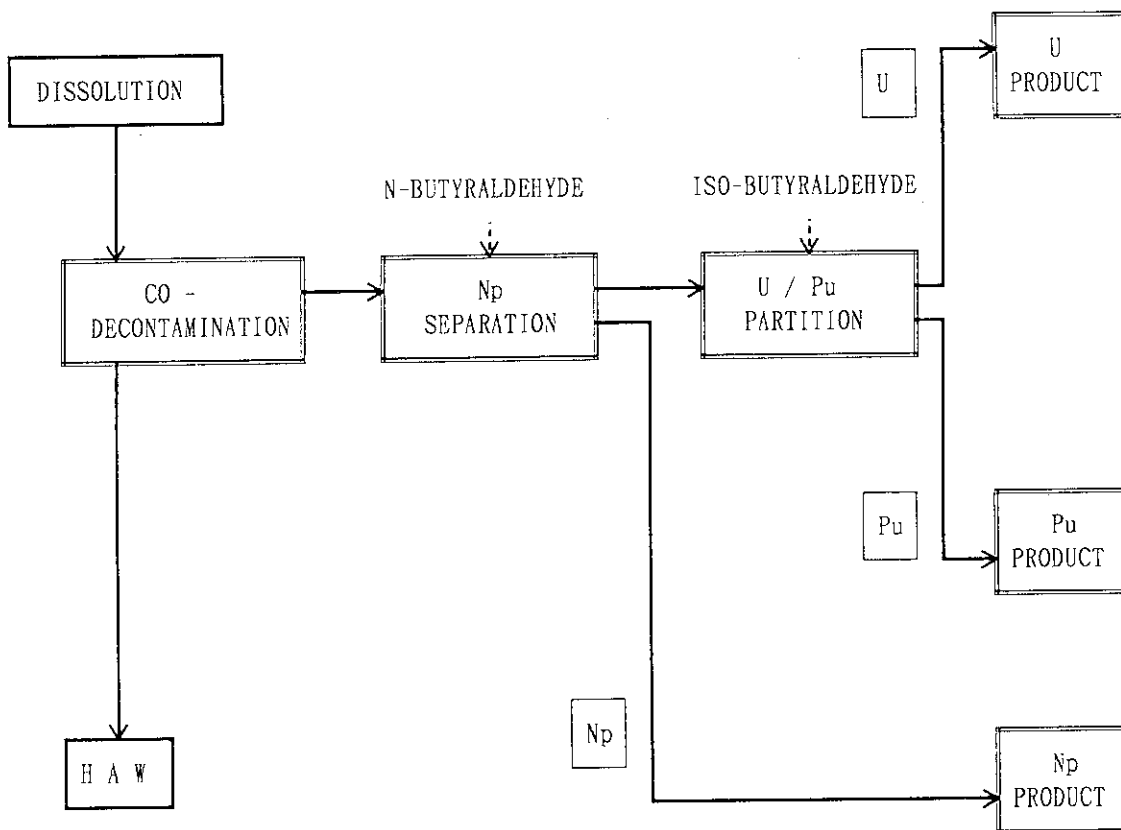


Fig. 13 New flow sheet by using n- and iso-butyraldehydes for Np/Pu/U separation.

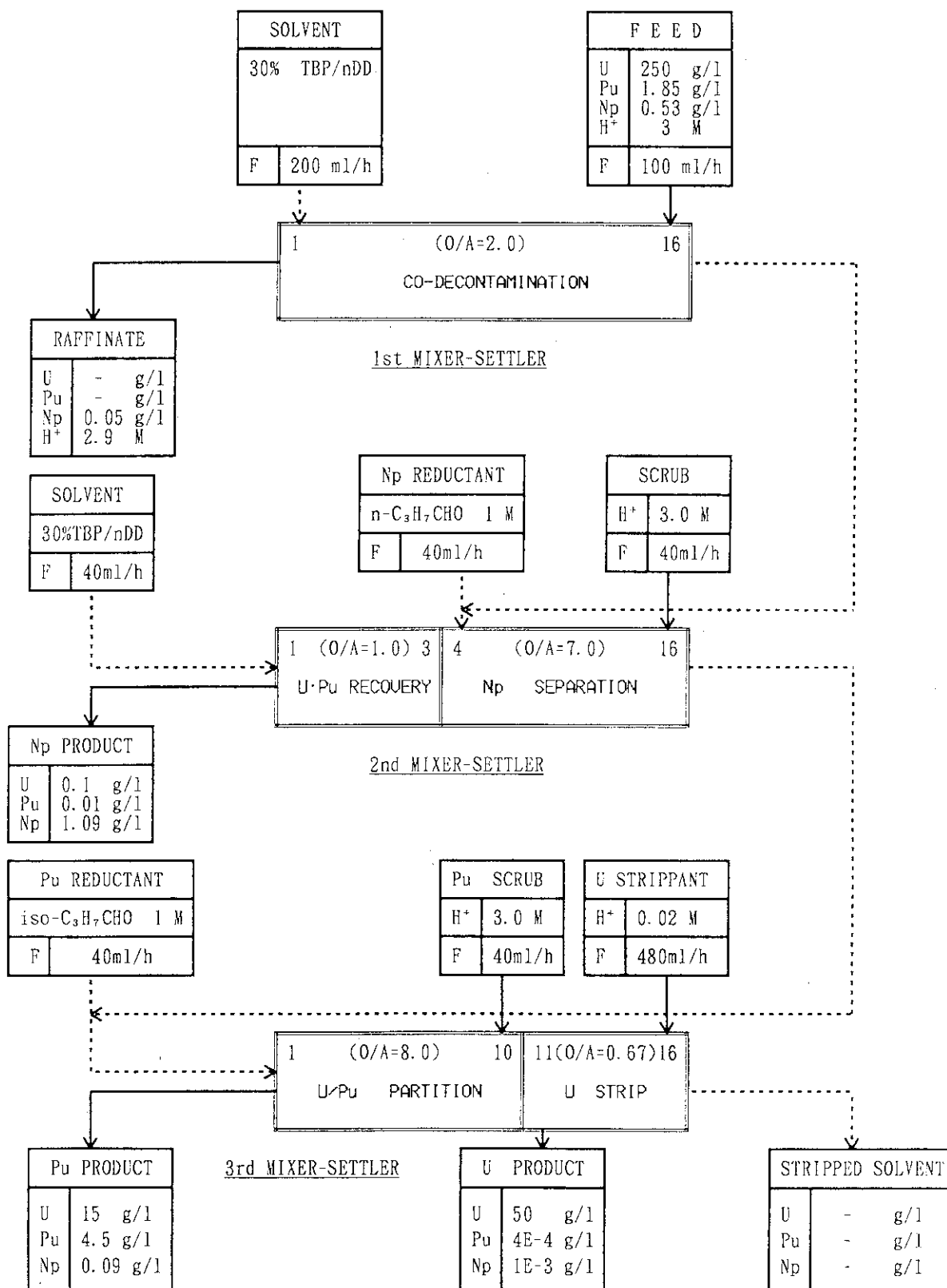


Fig. 14 Flow sheet of Run A and the concentrations of H⁺, Np, Pu and U in every stream.

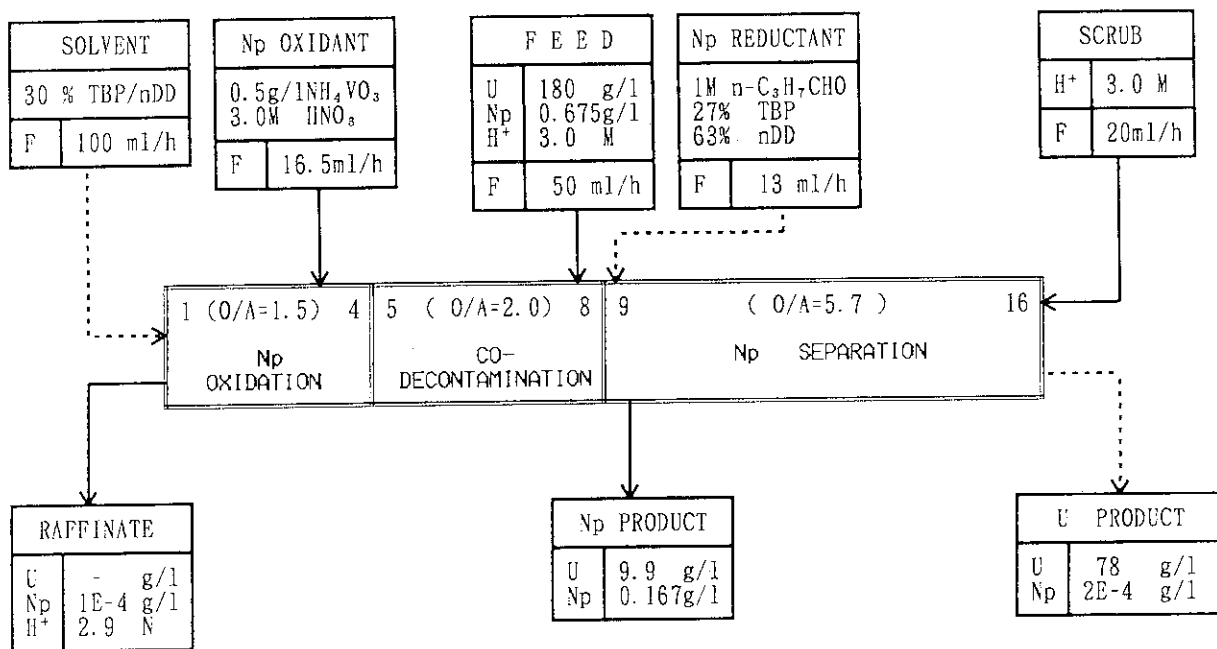


Fig. 15 Flow sheet of Run B and the concentrations of H⁺, Np, Pu and U in every stream.

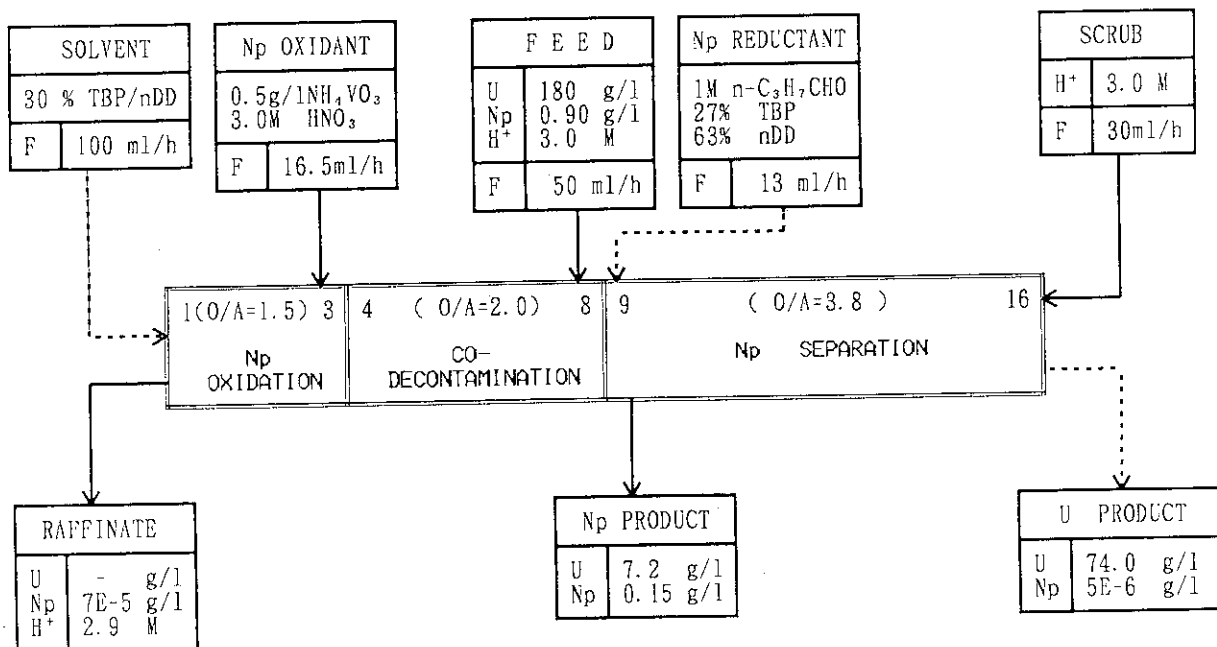


Fig. 16 Flow sheet of Run C and the concentrations of H⁺, Np, Pu and U in every stream.

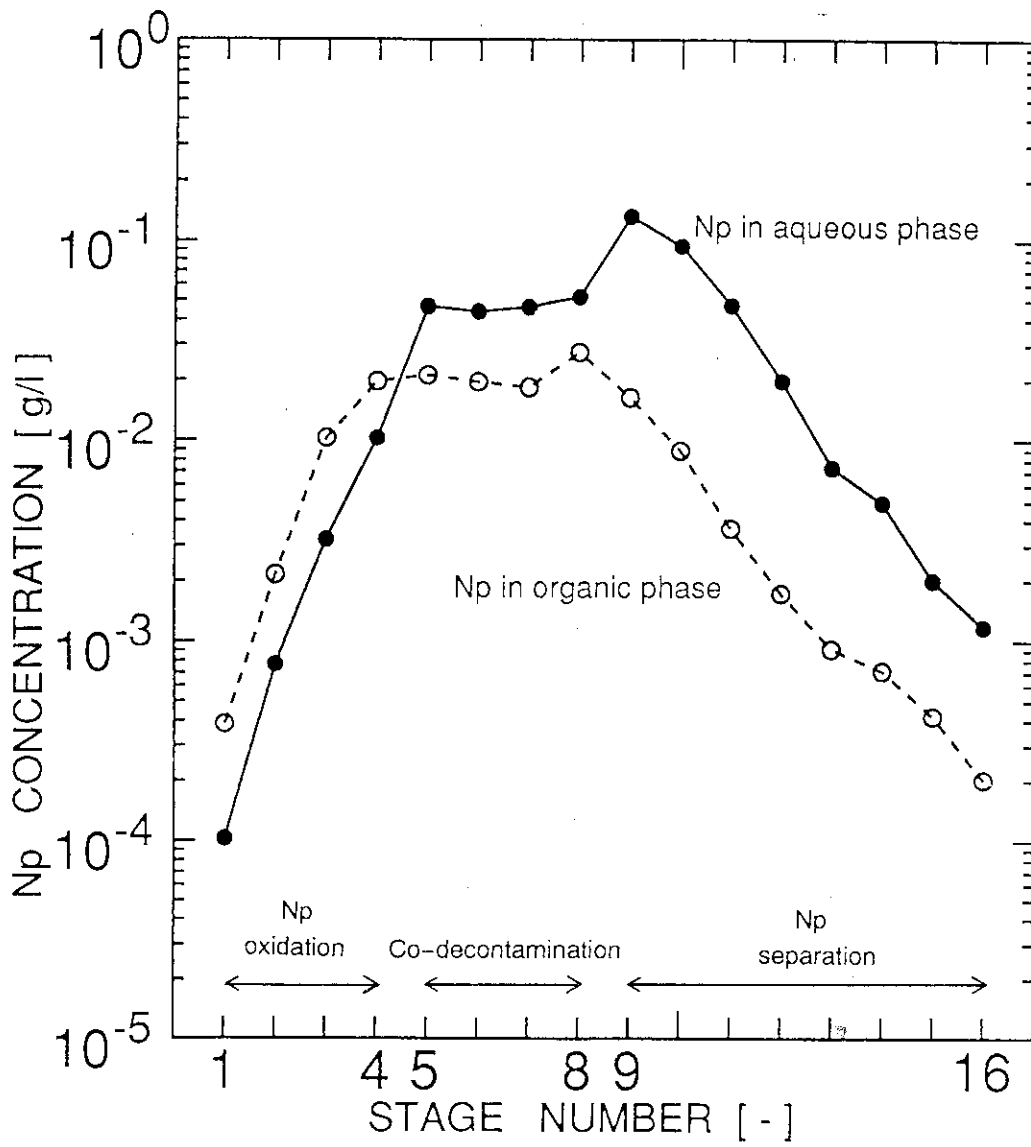


Fig. 17 Concentration profile of Np in the flow sheet study (Run B).

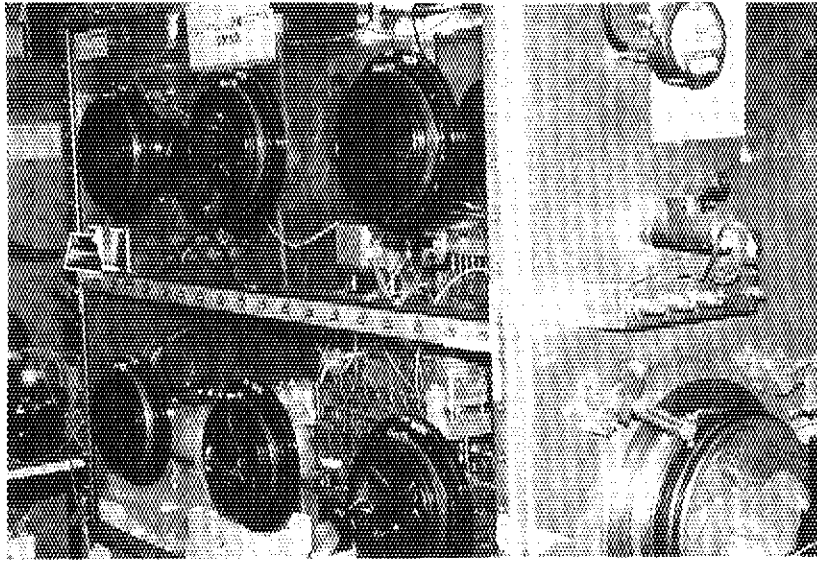


Photo. 1 Mixer-settlers in a glove box.

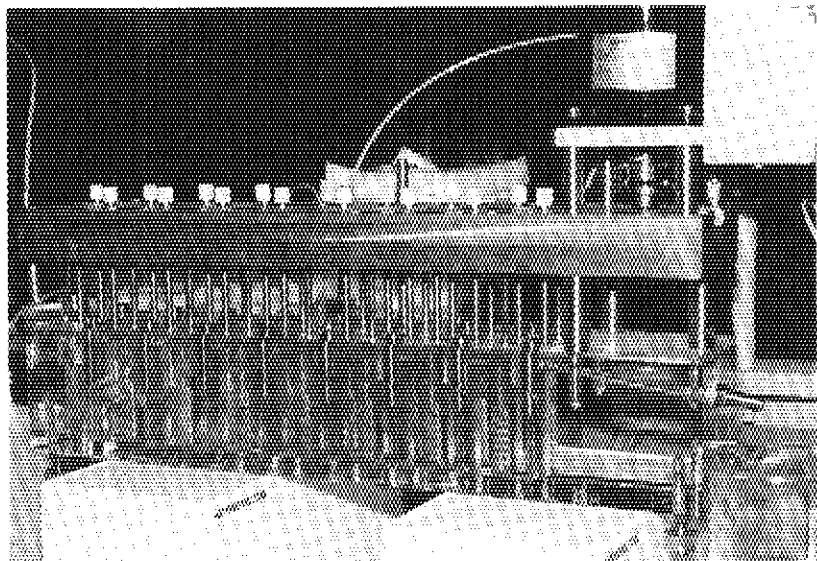


Photo. 2 Miniature mixer-settler of 16 stages.