Preliminary Study on the Partitioning of Transuranium Elements in High Level Liquid Waste

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1. BACKGROUND

In mid-seventies at the Tokai Works of the Power Reactor and Nuclear Fuel Development Corporation (PNC), a series of basic studies on separation of transuranium (TRU) elements from high level liquid waste (HLLW) was initiated as a part of broad R&D program on waste management technology. This effort, however, was halted in early eighties mainly because it became necessary to accelerate the R&Ds on vitrification technology and put more resources into them. Since then, a significant progress has been made in vitrification technology development, and the construction of the Tokai Vitrification Facility (TVF) has been well in progress on the site adjacent to the Tokai Reprocessing Plant (TRP). The TVF is a pilot-scale facility where the HLLW from TRP is vitrified using a liquid-fed ceramic melter (LFCM) system and the start of its cold check-out operation is scheduled to begin in the spring after next year.[1]

As illustrated in Fig. 1, the current reference scenario for dealing with the HLLW generated by spent fuel reprocessing is to solidify it into stable glass in stainless steel canisters and bury them in a geologic repository when their decay heat becomes low enough. [1] A time dependence of the toxicity of a typical high level waste is shown in Fig. 2. As indicated in other studies, the effect of fission products (FPs) such as Cs-137 and Sr-90 is dominant in the first few hundred years, but beyond one thousand years, TRU elements such as Am and Pu become main contributors even though their toxic level is relatively low. The low tail of toxicity continues for millions of years mainly due to Np-237 which has a half life around two million years.

The radiological safety to the environment and the public is ensured by the stability of glass and the isolation capability of both engineered and natural barriers. This method is considered to be a very practical way to safely dispose all the high level waste with negligible risk to the public. Many scientists and engineers in nuclear community agree that this can be done. In fact, our preliminary analysis indicates that the annual individual dose due to Np leaching-out and migration from forty thousand glass canisters buried in a deep ground repository is several order of magnitude

smaller than the natural background dose of 2 to 3 mSv/yr. In spite of this fact, quite unfortunately, we have not yet succeeded in convincing the public in the safety. One of the major reasons for not succeeding yet apparently comes from the simple fact that the high level waste itself does continue to be toxic for more than millions of years no matter how small the risk is.

Reflecting such situations, an option to recover ultra-long life TRU elements from the HLLW is being re-evaluated in conjunction with the technology to bum or convert them into isotopes with much shorter life. Along this line, we have resumed studies on partitioning of the TRU elements from the HLLW as a part of our long-term effort to widen the options in future waste management. In parallel with this effort, studies aimed for developing transmutation technology are also in progress in other parts of PNC and they are presented elsewhere in this specialists meeting.[2,3]

2. COMPOSITION OF HLLW

Concentrations of major FP and TRU elements in the HLLW from the TRP were measured and compared with those calculated with ORIGEN-II in Fig. 3. The measured to calculated ratios are significantly smaller than unity for some of the FP elements which tend to form insoluble residues and be trapped at the feed clarification process. The elements scattering near the unity in Fig. 3 are those which were completely collected in the HLLW. Among these are the rare earth FPs and the TRU elements such as Am and Cm. Our analysis also indicates that only 50 to 60 % of Np is collected in the HLLW and the remainder is considered to have gone mainly into the Pu product stream.[4] The leakage into the HLLW is usually about 0.1 % for uranium and 0.5 % or less for plutonium. In Fig. 4, the constituents in the HLLW were divided into three major groups; rare earth (RE) FPs, non-RE FPs and uranium plus TRU element group. For non-RE FPs, more than one third of the original inventory is removed as insoluble sludge in this figure. From this figure it is obvious that almost one half of the FPs in the HLLW are rare earth elements. Generally speaking, it is quite difficult in usual solvent extraction process to separate Am and Cm from rare earth group elements because both of them become tri-valent metal ions in nitric acid solution and behave in a very similar manner to each other.

If such HLLW is vitrified as it is, the time period for which the solidified waste remains more toxic than the natural uranium ore is estimated to be around 40,000 years (Fig. 2). On the other hand, if the majority of TRU elements are removed from the HLLW, this time period can be shorten from such a geological time scale down to the time scale of civilized human history. From our parametric study on the toxicity of high active wastes, it is indicated that the removal of Am by 99.9 % and Pu by 90 % is necessary so that the hazardous time period can be reduced

down to a few hundred years. The removal of Np and Cm by 90 % or more is desirable even though their removal is not crucial for the purpose of reducing this time period. Thus we can tentatively recommend a goal decontamination factor of 103 for Am, 10 for Pu, and 102 if achievable for Np and Cm.

3. FUNDAMENTAL APPROACH OF TRU REMOVAL STUDY

Our current study on removal of TRU elements from the HLLW consists of two parallel efforts as shown in Fig. 5; a study on the method of controlling Np in existing PUREX process so that the Np will not come into the HLLW, and a study to recover remaining TRU elements from the HLLW.

In the current PUREX process in the TRP, the Np is almost completely extracted into the organic solvent (30% TBP in *n*-dodecane) in the first extraction cycle. However, only 40 to 50 % of Np is extracted into the solvent in the second cycle and the remainder (50 to 60 %) goes into the raffinate which composes a part of the HLLW.[4] Since Np-239 is burnable in the reactor, especially in the fast flux reactor, one favorable option is to send most ofl Np into the Pu stream and minimize. its leakage into the raffinate or HLLW. The concept of this option (i.e. "advanced" PUREX process) is compared with the cm-rent PUREX process in Fig. 6.

In order to control the behavior of Np in the PUREX process, it is necessary to adjust its valency into a right state. It is well known that penta-valent ion Np(V) is non-extractable into TBP solvent whereas other forms on neptinium ions Np(IV) and Np(VI) are easily extractable. A traditional method for adjusting valency of neptinium ions is to use some oxidizing or reducing reagents depending on the situation. We are now seeking the way to adjust Np valency by not using chemicals but by using electrolysis or photochemical reaction induced by ultraviolet light or laser. The work on photochemical process is reported in the other session of this meeting.[5]

4. PRELIMINARY STUDY ON TRU SEPARATION FROM THE HLLW

With regard to the method for separaing the TRU elements from the HLLW, we are primarily seeking the solvent extraction process which is compatible with the existing PUREX process. From such point of view, neutral phosphate extractants are preferable because they do not require a pretreatment such as a denigration for the HLLW. At present, two candidate solvents of this category shown in Fig. 7 are being evaluated for use in TRU separation from the HLLW. The di-butyl butyl phosphonate (DBBP) is the extractant we examined in our early study and a fairly good amount of base data has been accumulated for this. The octyl phenyl-*n n*-di-isobutyl-carbamoyl methylphosphine oxide (CMPO) is a bifunctional

organophosphoric extractant which was invented by Argonne National Laboratory (ANL) in their TRUEX Process.[6] Our near-term objective is to evaluate characteristics of the TRU separation processes with these extractants and identify the flowsheet worthy to continue R&Ds for further steps as shown in Fig. 8.

(Preliminary Study on DBBP Process)

Distribution equilibrium constants of the TRU elements and some typical FP elements were measured and compared among several extractants in Table-1. It is indicated in the table that the DBBP has not the best but a fairly good capability to extract tri-valent metal ions such as Am and Cm which are hard to extract into the TBP. The distribution constant for Ce, one of the rare earth FPs, is quite similar to those for Am and Cm. The non-rare earth FPs such as Cs and Sr are not extractable into the DBBP whereas U and Pu have very high distribution constants.

One of the demerits of the DBBP method is that it is necessary to use several completing and salting-out reagents to make this process work efficiently. However, it is a very attractive point of this extractant that the separation of the TRU elements from the rare earth FPs seems possible by using a completing reagent DTPA in a strip solution. The DTPA is a completing reagent used in the Talspeak process once studied at the Oak Ridge National Laboratory (ORNL). In our preliminary study, Am was used as a typical TRU element and Ce as a typical rare earth element, and their stripping characteristics from 30 % DBBP in *n*-dodecane were examined by using 0.05 M DTPA in 1 M lactic acid as a strip solution. It was indicated in Fig. 8 that both Am and Ce were very easy to strip from the solvent but their distribution ratios were almost the same for the pH range from 1 to 5. In other words, these two elements were almost impossible to separate from each other in the case where the strip solution is free of NO_3^-. However, the difference of distribution ratio became quite remarkable between these two elements when NO_3^- was added into the strip solution as 0.5 M $Al(NO_3)_3$ as shown in Fig. 8. In the latter case, the separation factor is nearly equal to 10 in the pH range around 2 with the distribution ratio slightly larger than 1 for Ce and about 0.1 for Am. In this case, the addition of NO_3^- resulted in the formation $Ce(NO_3)_3$ which is apt to be retained in the DBBP by forming a complex.

(Preliminary Study on CMPO and TRUEX Process)

A series of cold beaker tests to verify basic characteristics of the CMPO solvent was conducted by using Ce to simulate tri-valent TRU elements, and Rh and Zr as typical non-RE FPs. The solvent used was a mixture of 0.2M CMPO in TBP/*n*-dodecane. Preliminary results were summarized in Fig. 9. The distribution ratio for Ce was determined to be higher than 1

where it was around one tenth for Rh. The distribution ratio measured for Zr was in the order of 102 but it was lowered by three orders of the magnitude when a small amount of oxalic acid was added. Other elements were quite insensitive to the presence of oxalic acid. A very high distribution ratio was obtained for U. The distribution ratios for these elements showed very small dependence on the acidity above 1 molar. These results generally agree with the data shown in published reports.[7]

Batch shaker tests with actual high level waste solution generated from the hot reprocessing test are in progress at the Chemical Processing Facility (CPF) in the PNC Tokai Works. Distribution ratios measured for several FP elements were summarized in Fig. 10. Tests are being continued to obtain distribution data for major TRU elements.

At present, efforts to accumulate such basic data with the CMPO extractant are being continued and the first hot test run with small-scale mixer-settlers has been recently conducted to evaluate the characteristics of the basic TRUEX flowsheet. Major R&D items were summarized in Fig. 11 for comprehensive assessment of the TRUEX process and its improvement.

5. CONCLUSION

The status of the preliminary study on TRU partitioning from the HLLW at the PNC Tokai Works has been reviewed. As a part of efforts in developing "advanced" PUREX process, methods to control Np are being studied so that most of Np will be sent into the Pu product stream and its leakage into the HLLW is minimized. As for the method for separating TRU elements from the HLLW, both DBBp and CMPO are now being examined as candidate extractants in basic experiments with batch shakers or small-scale mixer-settlers. By accumulating basic data from such experiments, an overall assessment of the process and technology for TRU partitioning will be made in near future.

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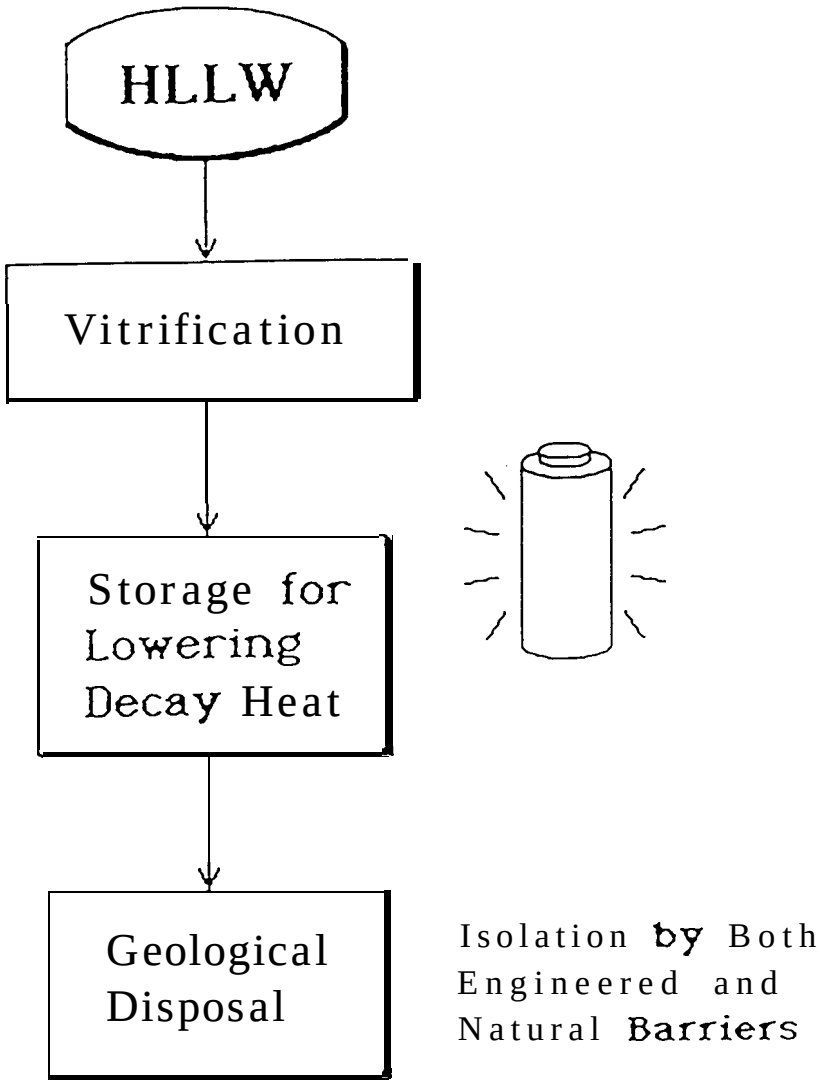


Fig. 1 REFERENCE SCENARIO FOR HLLW TREATMENT AND DISPOSAL

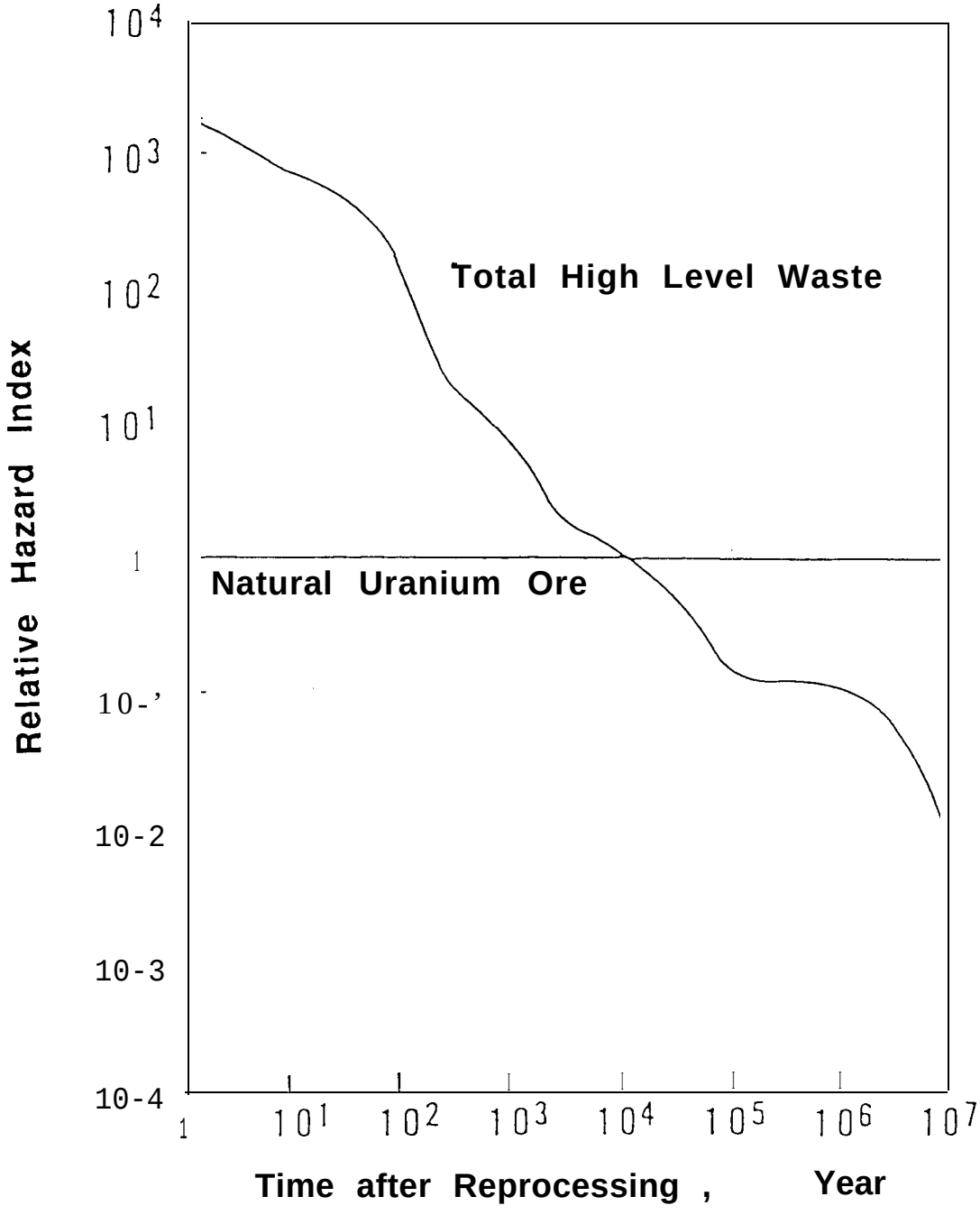


Fig. 2 RELATIVE HAZARD INDEX OF VITRIFIED HIGH LEVEL WASTE

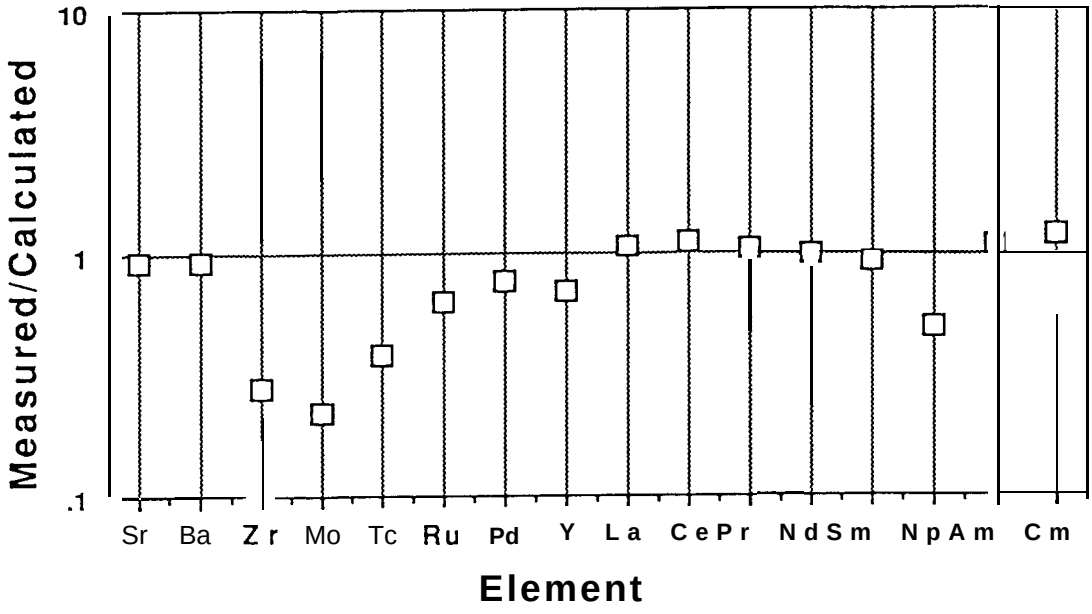


Fig.3 **CHEMICAL COMPOSITION OF HLLW IN TRP COMPARED WITH ORIGEN CALCULATION**

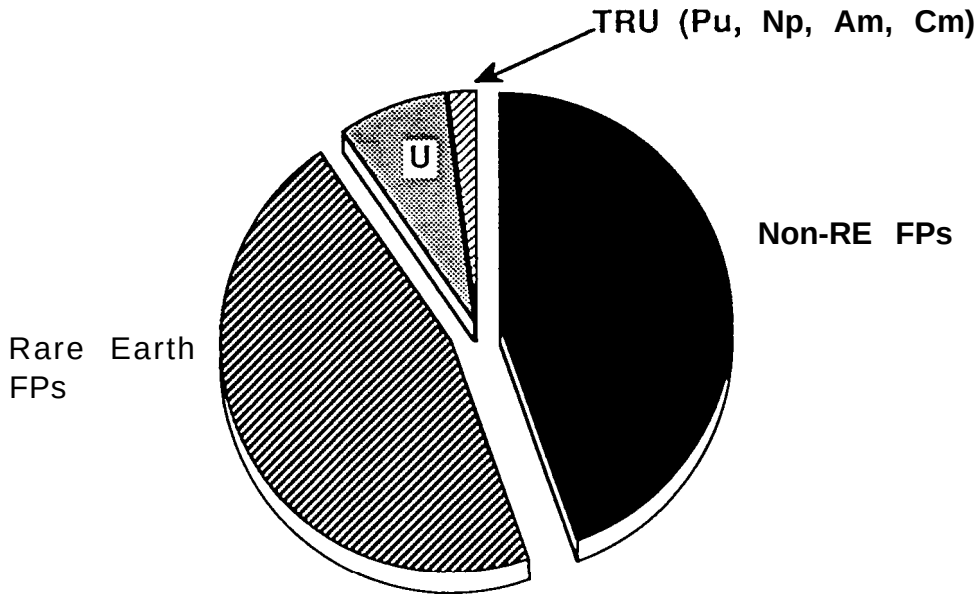


Fig.4 COMPOSITION OF HLLW IN TRP

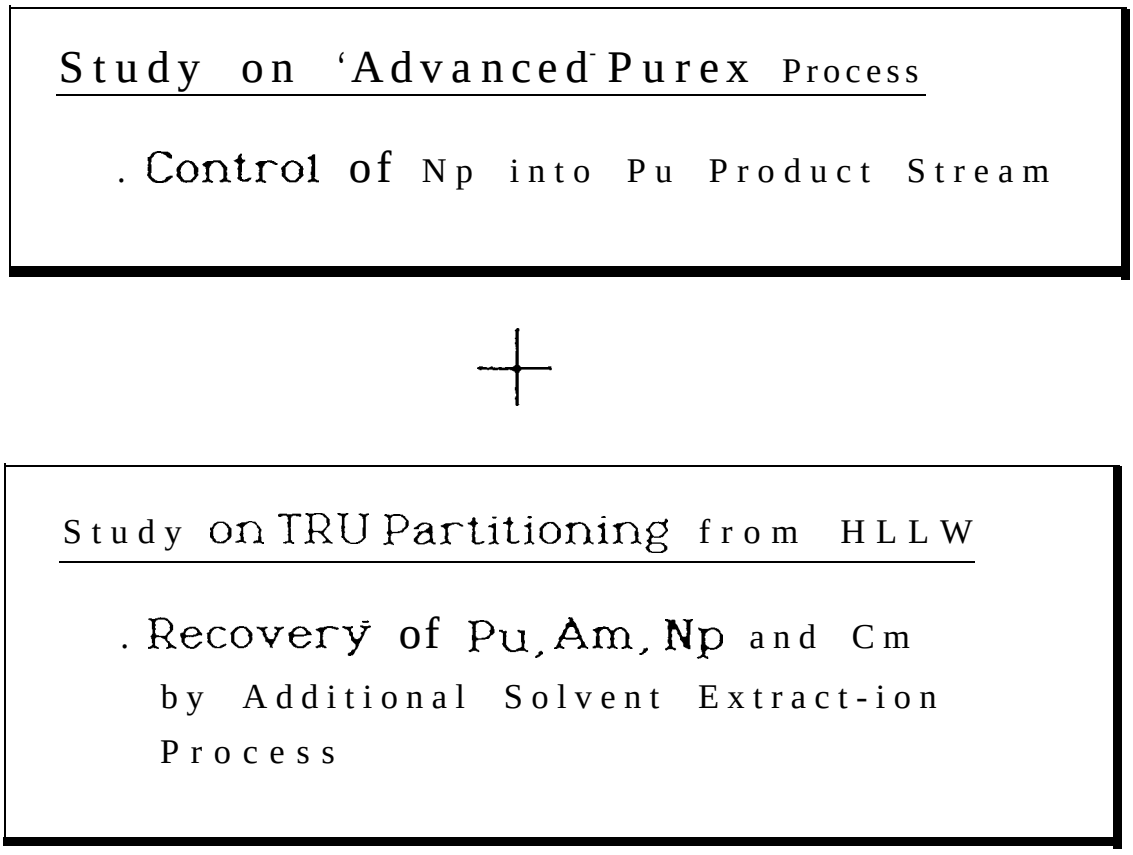


Fig. 5 GENERAL SCOPE OF STUDY ON TRU REMOVAL FROM HLLW

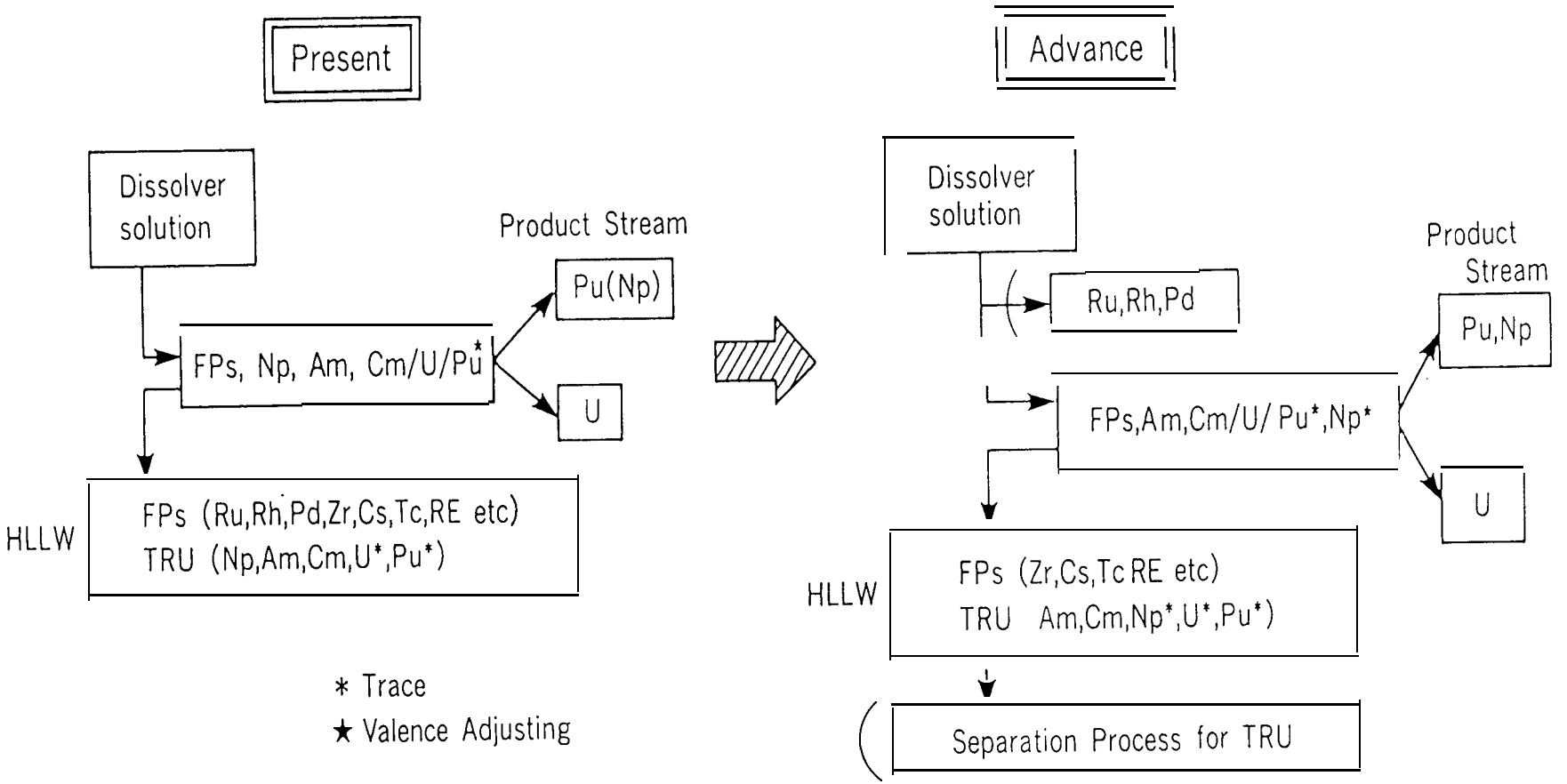
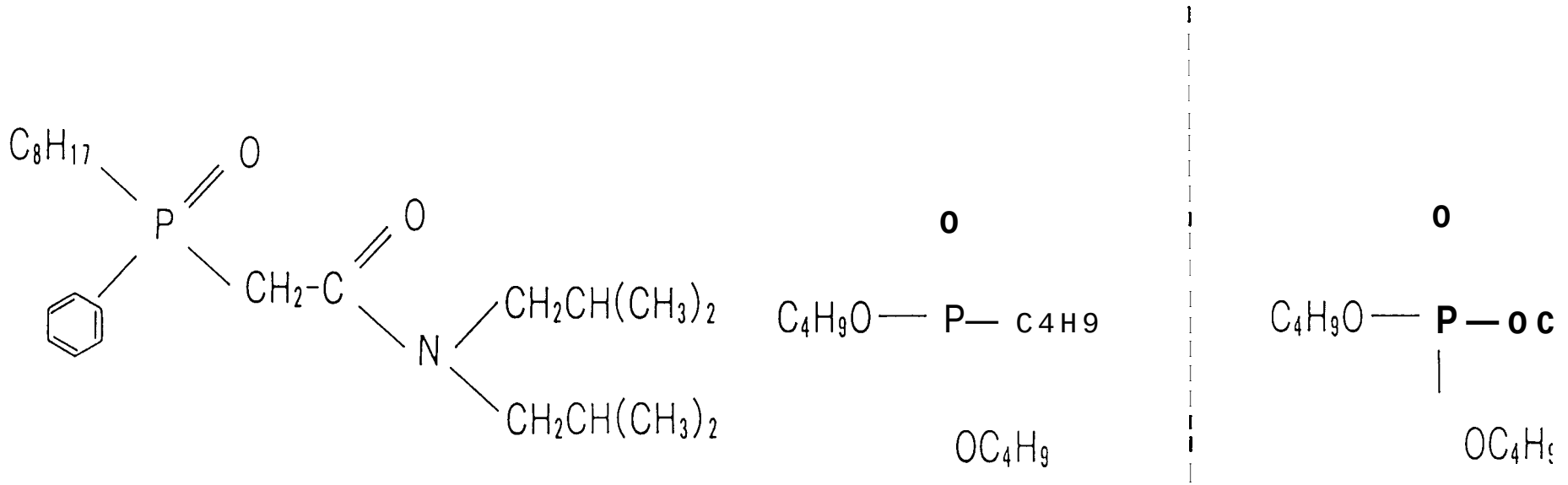


Fig. 6 "ADVANCED' PUREX PROCESS



Octyl(Phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide
OΦD(IB)CMPO

Dibutyl butyl phosphonate
DBBP

TBP

Fig. 7 CANDIDATE EXTRACTANTS FOR TYPICAL TRU SEPARATION PROCESS

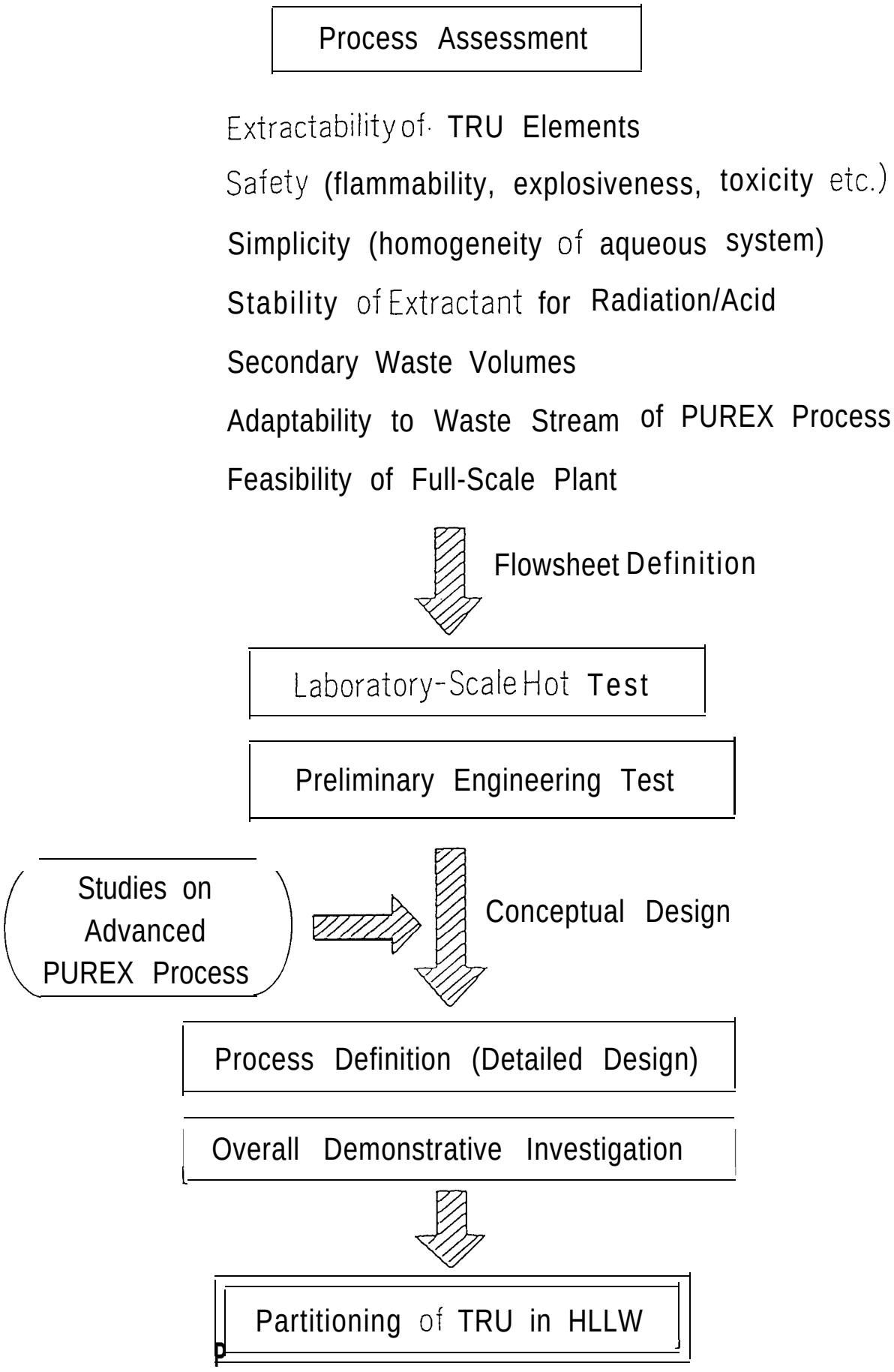


Fig. 8 STEPS FOR DEVELOPING TRU SEPARATION PROCESS

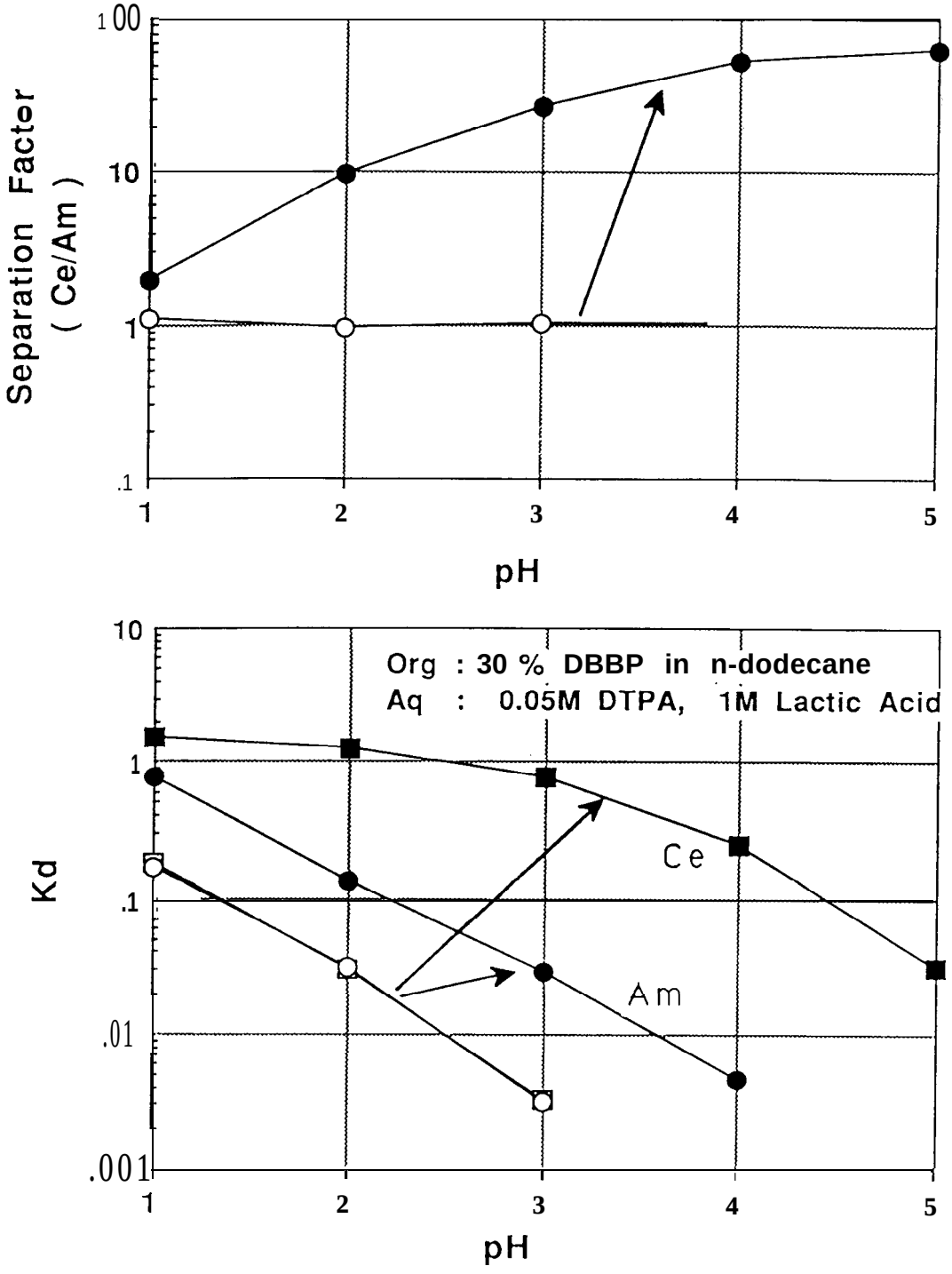


Fig. 9 CHANGE OF DISTRIBUTION RATIOS BY ADDITION OF 0.5M $Al(NO_3)_3$

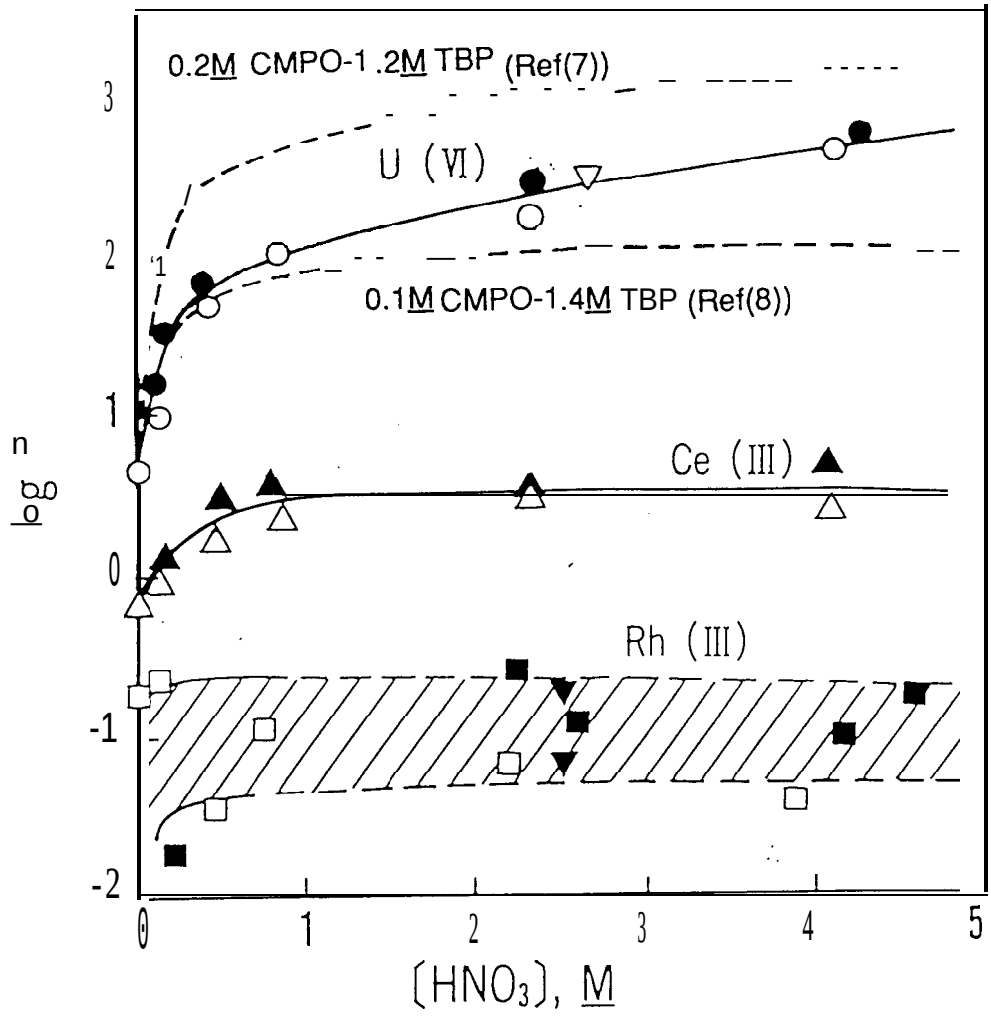


Fig. 10 ACID DEPENDENCY OF Du, D_{Ce} and D_{Rh} WITH 0.2M CMPO AND 1.4M TBP IN n-DOD ECANE

0.2M CMPO-1.4M TBP in DD
Room temp.

○ : U (Vi)
● : U (VI) + $H_2C_2O_4$ (0.03M)
△ : Ce (III),
A : Ce(III) + $H_2C_2O_4$ (0.002~0.03M)
❑ I:Rh (III)
❑ : Rh (III) + $H_2C_2O_4$ (0.03~0.2M)
▽ : Zr (Iv)
▼ : Zr (Iv) + $H_2C_2O_4$ (003 -o. .2M)

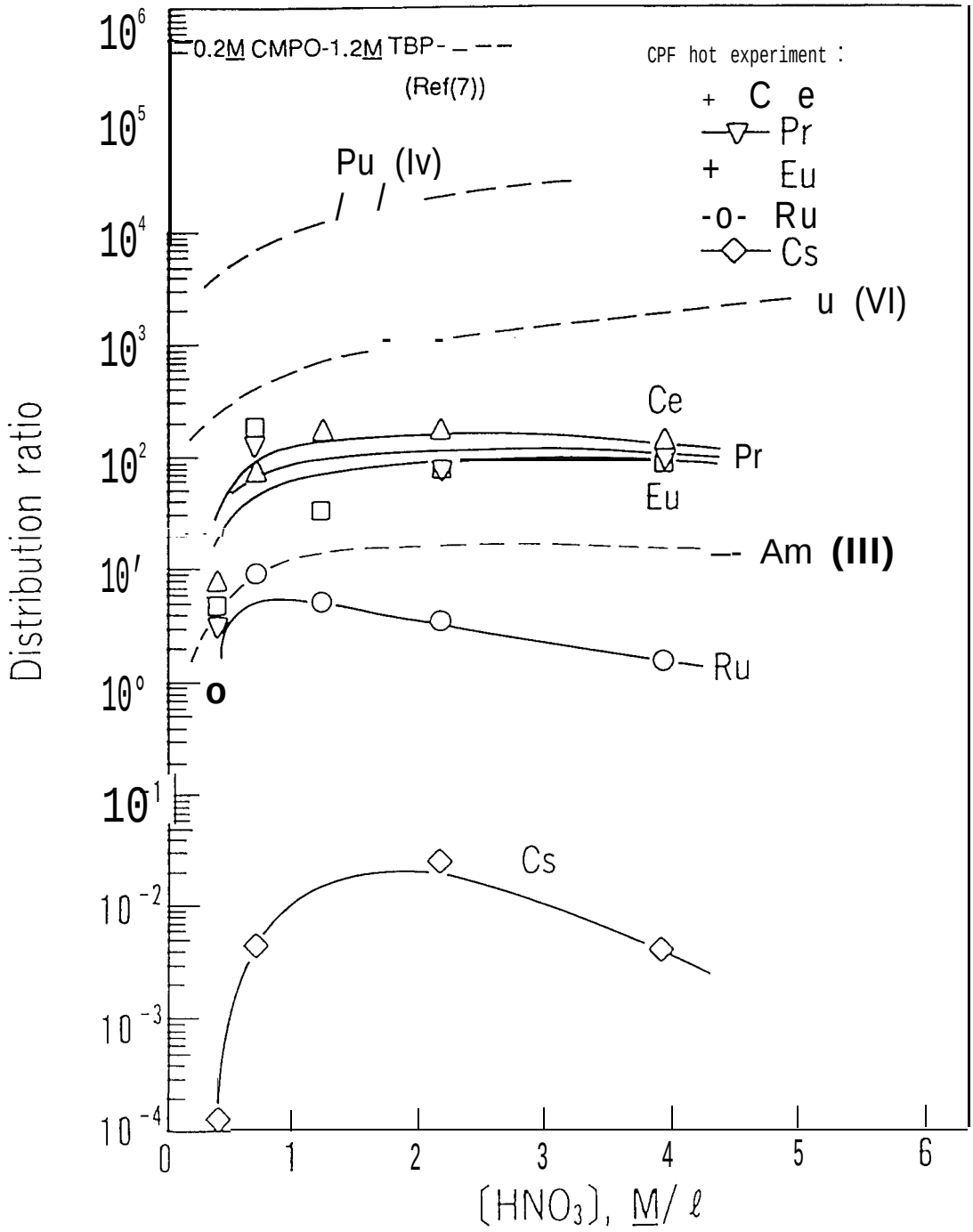


Fig. 11 ACID DEPENDENCY OF D_{TRU}, D_{RE} and D_{Cs} WITH 0.2M CMPO AND 1.0M TBP IN N-DODECANE

Major R&Ds on the TRUEX process

Fundamental aspect

- Confirm separation factor of TRU from HLLW using general TRUEX flowsheet
- Identify extraction mechanism between CMPO and metal ions
- Improve TRUEX flowsheet
  - Increase separation factor of FPs and back extraction efficiency of TRU, especially necessity of addition the complex compound such as carboxylic acid
  - Increase extractability of Np and Tc
  - Confirm third phase formation region
- Solvent degradation
  - Hydrolysis, Radiololysis
  - Solvent cleanup.
- Raffinate wash
  - Diluent washing or steam stripping
- TRU/Rare-earth nuclides separation method
  - Necessity
  - Feasibility

Engineering aspect

- Equipment development
  - Centrifugal contactor or another method
- Process control

Fig. 12 MAJOR R&Ds ON THE TRUEX PROCESS

Table-1 APPARENT DISTRIBUTION EQUIBRIUM CONSTANTS

Extractant	Am	Cm	Ce	Pu	U	Sr	Cs
DBBP	6.23	7.68	5.86	ca. E+2	ca. E+3	*	*
TBP	3.52E-2	5,49 E-2	3.12E-2	2	11	*	*
HDEHP	8.45E-1			**	**	1.3E-4	1. 1E-4
HDEHP-mixture	22	22.7	18.6	**	**	5,52 E-2	1.17E-1

* Negligible

. Large