

NEPTUNIUM AND TECHNETIUM CONTROL IN REPROCESSING

Sachio FUJINE, Gunzo UCHIYAMA, Mitsuru MAEDA
Japan Atomic Energy Research Institute(JAERI)

Abstract

A concept of the modified Purex reprocessing incorporated with partitioning is proposed for the purpose of enhancing the efficiency of long-lived nuclides control in the future. Not only long-lived actinides but also long-lived fission products are taken into account in the process concept. The process is expected to reduce the long-term toxicity and the volume of radioactive waste as well as the radioactivity released to the environment as low as reasonably achievable. Separation of the extractable Np-237 and Tc-99 has been demonstrated by the modified Purex extraction process using salt-free reagents of butyraldehyde. A new experimental equipment, which has been installed in a $\alpha \gamma$ cell, is going to be introduced for the feasibility study of the modified Purex process; PARC process.

INTRODUCTION

Plutonium recycle without the integration of long-lived nuclides is the ideal concept of the nuclear power supply system in the future. The centralized large scale reprocessing facility for LWR fuels in the future is expected to reprocess the advanced fuels which contain more actinides and fission products than the present fuel¹⁾. Plutonium recovery rate must be kept at the high level and must be improved further in the future. The increase of Am and Cm content in the spent fuels leads to the increase of heat generation and neutron discharge in high level liquid waste (HLW) of reprocessing. The extractable long-lived Np-237 (The half-life is 2.14×10^6 years.) and Tc-99 (The half-life is 2.11×10^5 years.) require much effort to purify the U and Pu products in the solvent extraction cycles.

The reprocessing in the future should have the advantages of reducing the long-term toxicity of radioactive waste, reducing the volume of the waste, and also reducing the radioactivity released to the environment as low as reasonably achievable. Attention must be paid not only to the long-lived actinides but also to the long-lived fission products, because the volatile long-lived C-14 (The half-life is 5.73×10^3 years.) and I-129 (The half-life is 1.57×10^7 years.) are easy to be released to the environment from normal operation of the reprocessing plant. Those long-lived fission products are assessed to have the relatively bigger effect on the collective dose rather than the minor long-lived actinides²⁾. From those points of view, we made a concept of advanced reprocessing incorporated with partitioning; PARC process. Long-lived nuclides are separated and isolated in the process.

CONCEPT OF ADVANCED REPROCESSING

A modified Purex process incorporated with partitioning may be illustrated as the block flow diagram shown in Fig.1. Plutonium and uranium are decontaminated in a single extraction cycle. Plutonium recovery rate is enhanced by optimizing the operation condition, although the decontamination factor of Pu may be slightly lower than the standard 3 extraction cycle process. The recovered Pu may contain a part of U and Np. Long-lived nuclides such as C-14, I-129, Tc-99 and Np-237 are controlled in the reprocessing. Undissolved residue which contains approximately 30% Tc is not mixed in HLW. Am and Cm, which have leaked out to the raffinate, are assumed to be recovered from the raffinate. As the long-lived actinides, Np-237, Pu-239, Pu-240, Am-241, Am-243 and Cm-244 must be considered. Half-life on Np-237 is 2.14×10^6 years. Half-lives of the other actinides are 2.41×10^4 years for Pu-239, 6.58×10^3 years for Pu-240, 7.95×10^3 years for Am-243. Half-life of Am-241 is not long, but, it decays to long-lived Np-237 by half-life of 458 years. Long-lived Am-243 decays by half-life of 7.95×10^3 years to long-lived Pu-239. Cm-244 decays to long-lived Pu-240 by half-life of 17.6 years.

An assessment of the collective dose due to the radioactivity released both to the atmosphere and to the ocean from a reprocessing plant shows that C-14, I-129, Pu-239 and Pu-240 among the above mentioned long-lived nuclides take a big part of the dose²⁾. The effect of Np-237 and Tc-99 on the collective dose is assessed to be relatively small. However, those nuclides are extractable to the extractant TBP. Much effort is required to remove Np-237 and Tc-99 from the U and Pu products in the extraction process of reprocessing. The extraction process is forced to be complicated to remove and confine those dispersed elements. A high efficient technology of controlling Np and Tc must have a big advantage of simplifying the purification processes and reducing the waste volume contaminated with those long-lived nuclides. Separation of those nuclides in reprocessing helps reducing the burden of partitioning those nuclides from HLW. Those nuclides have high potential as the hazardous elements because they have the chemical property of fast dispersion in the environment if the confining barrier is eroded. Np and Tc are expected to be separated in the purified condition in the modified reprocessing

Our concern on the long-lived nuclide control in reprocessing is summarized as follows,

- Remove C-14 and I-129 from the off-gas
- Enhance Pu recovery rate
- Separate the extractable Np and Tc
- Recover the inextractable TRU elements: Am and Cm.

SEPARATION PROCESS OF Np, Tc, Pu AND U USING BUTYRALDEHYDES AS SALT-FREE REDUCTANTS

Valency control technique takes the important role to control the elements behaviour in the extraction process. Valency changes depending on electric potential of the liquid. Reducing reagents are effective to control the electric potential homogeneously of the solution in a large scale contactor. Those reagents must be decomposable to gas and water, namely, salt-free. Otherwise, the volume of α contaminated waste will be increased. Butyraldehyde is one of the salt-free reagents. Butyraldehyde has isomers. The redox potentials of normal- and iso-butyraldehydes in 3M HNO₃ at 25°C are app.0.72 and 0.66 V versus saturated calomel electrode, respectively. The potential of n-butyraldehyde is much higher than the standard redox potential of the U(VI)-U(IV) system, a little higher than that of the Pu(IV)-Pu(III) system, and lower than that of the Np(VI)-Np(V) system. The potential of iso-butyraldehyde is a little lower than that of the Pu(IV)-Pu(III) system.

Normal-butylaldehyde reduces hexa-valent Np selectively. Iso-butylaldehyde reduces hexa-valent Np and tetra-valent Pu as well. Normal-butylaldehyde has much higher selectivity and a much lower reaction rate than iso-butylaldehyde. The results of the kinetics study(Fig.2) show that n-butylaldehyde reduces Np(VI) to Np(V) in the Purex solution but does not reduce Pu(IV) and U(VI), and iso-butylaldehyde reduces Np(VI) and Pu(IV) but does not reduce U(VI)⁹.

Inter-element separation of U, Pu and Np is possible by using normal- and iso- butylaldehyde properly. Feasibility study of a new process has been conducted to separate Np, Pu and U, selectively. Stripping Np from the solvent before the U/Pu partition step is considered to be favorable to prevent Np from diffusing into the downstreams. A proposed process, shown in Fig.3, consists mainly of three steps: a codecontamination(coextraction) step, a Np separation step using n-butylaldehyde, and a U/Pu partition step using iso-butylaldehyde as a Pu(IV) reductant. Hexa-valent Np(VI) ions, which is extracted by 30%TBP/n-dodecane solvent together with Pu(IV) and U(VI), are reduced and back-extracted from the solvent. Leakage of Np to the raffinate is prevented by the inserted oxidation step to the codecontamination step. Ammonium vanadate were employed in the experiment. The effectiveness of the separation process is demonstrated in the chemical flow sheet study using miniature mixer-settlers. In the Np separation step, app. 99.98% of the Np, which is extracted by 30%TBP/n-dodecane solvent along with U(VI) in the coextraction step, is reduced by n-butylaldehyde and separated from the uranium stream. In the U/Pu partition step, over 99% of the plutonium is reduced by iso-butylaldehyde and separated from the uranium stream. Pu(IV) is effectively reduced by iso-butylaldehyde without hydrazine as nitrous acid decomposing reagent. Figure 4 shows one of the result of flow sheet experiment.

Technetium can be separated along with neptunium by n-butylaldehyde. Experimental study is under way to optimize the operation condition to separate both Tc and Np in a proposed process.

STUDY ON MINOR ACTINIDES RECOVERY

Oxidation step was needed to increase the recovery rate of Np from the raffinate of codecontamination step. Salt free reagent is preferable, although non-salt free reagent, ammonium vanadate, was used in the experiment of Np recovery process. We will study salt-free methods to oxidize minor actinides in the raffinate to the higher valent states which are extractable to TBP. The calculation result(Fig.5) under a simple condition shows much higher electric potential is needed to change the tri-valent Am to the higher valency states than that is needed to change penta-valent Np to the extractable hexa-valent state. Unfavorable reactions caused by the high electric potential must be avoided.

NEW EXPERIMENTAL FACILITY

A bench scale experimental equipments for dissolution, off-gas treatment, extraction and liquid waste recycling process has been installed in $\alpha \gamma$ cell of BECKY facility in NUCEF(Nuclear Fuel Cycle Safety Engineering Research Facility)⁴⁾. High burnup spent fuel specimens(Max.3kg/year) will be transferred to the cell after chopped at the outside of the facility. Main flow sheet is shown in Fig.6. Acid test is undergoing. Uranium test is scheduled to start in the spring of 1995. Study on reprocessing consists of five subjects:(1)Kinetics of continuous dissolution of spent fuel and collection of basic data on the solubility of spent fuel, (2)The simplified reprocessing incorporated with partitioning, (3)Demonstration on the confinement of radioactive nuclides in reprocessing process, (4)Development of process simulation code system, (5)Iodine and carbon-14 confinement technology by dry process.

The outcomes of those research will be applied to the development of an advanced reprocessing incorporated with partitioning(PUREX-integrated partitioning system). Study on the volatile I-129 and C-14 is to understand their behaviour in the dissolution and to develop a dry technology to reduce those long-lived nuclides as low as reasonably achievable. Some new adsorbents are scheduled to be tested on the efficiency of removing iodine and carbon oxide. A simulation code system ARECS, as shown in Fig.7, is under development to understand the behaviour of long-lived nuclides in the dissolution, off-gas treatment and extraction steps of a reprocessing process for LWR⁵⁾, aiming at the improvement of the efficiency of the long-lived nuclides control. The simulation codes will be verified and improved through analyzing the data obtained from the experiment in $\alpha \gamma$ cell.

As a goal of the process concept of the advanced reprocessing incorporated with partitioning, we have made a block flow diagram of PARC process, as shown in Fig.8, taking into account of the past study⁶⁾. The combined work of the experimental study and analysis by the simulation code is expected to show the way to the goal of PARC process through modifying the present Purex process.

CLOSING REMARK

In the history of the development of reprocessing technology, much effort has been made on reducing the radioactivity released to the environment. The new effort of reducing the volume and long-term toxicity of the radioactive waste by controlling long-lived nuclides is expected to lead us to a new standard of the confinement of radioactivity. We think that the concept of the modified Purex reprocessing incorporated with partitioning is the practical way to achieve the new standard in the future.

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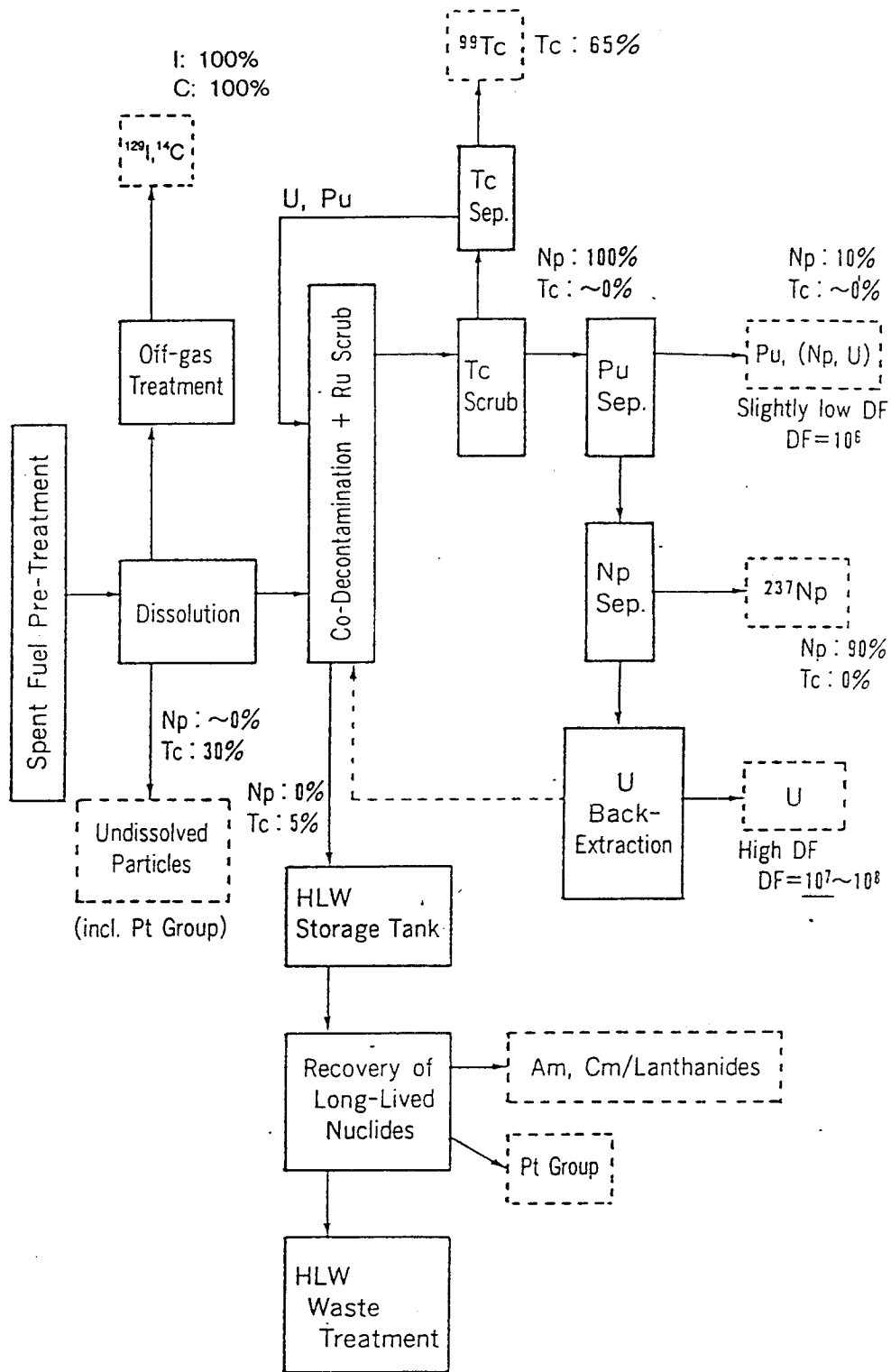


Fig.1 A conceptual block flow diagram of the advanced reprocessing incorporated with partitioning.

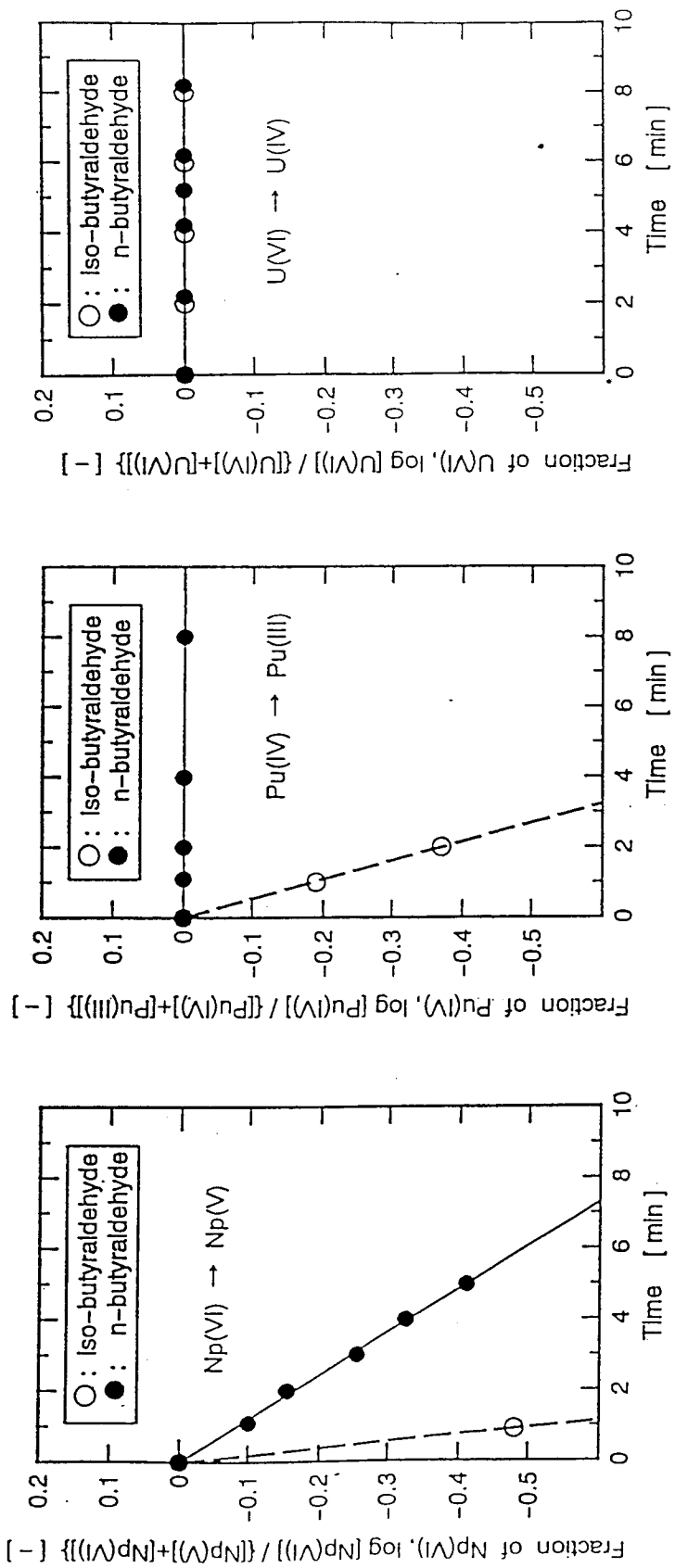


Fig.2 A result of kinetics study; Time dependency of fractions of Np(VI), Pu(VI) and U(VI) under the reduction reaction by normal- and iso-butyraldehydes, Np(VI):0.13g/l, Pu(VI):5.5g/l, U(VI):20g/l, H⁺:3M, Temperature:293K.

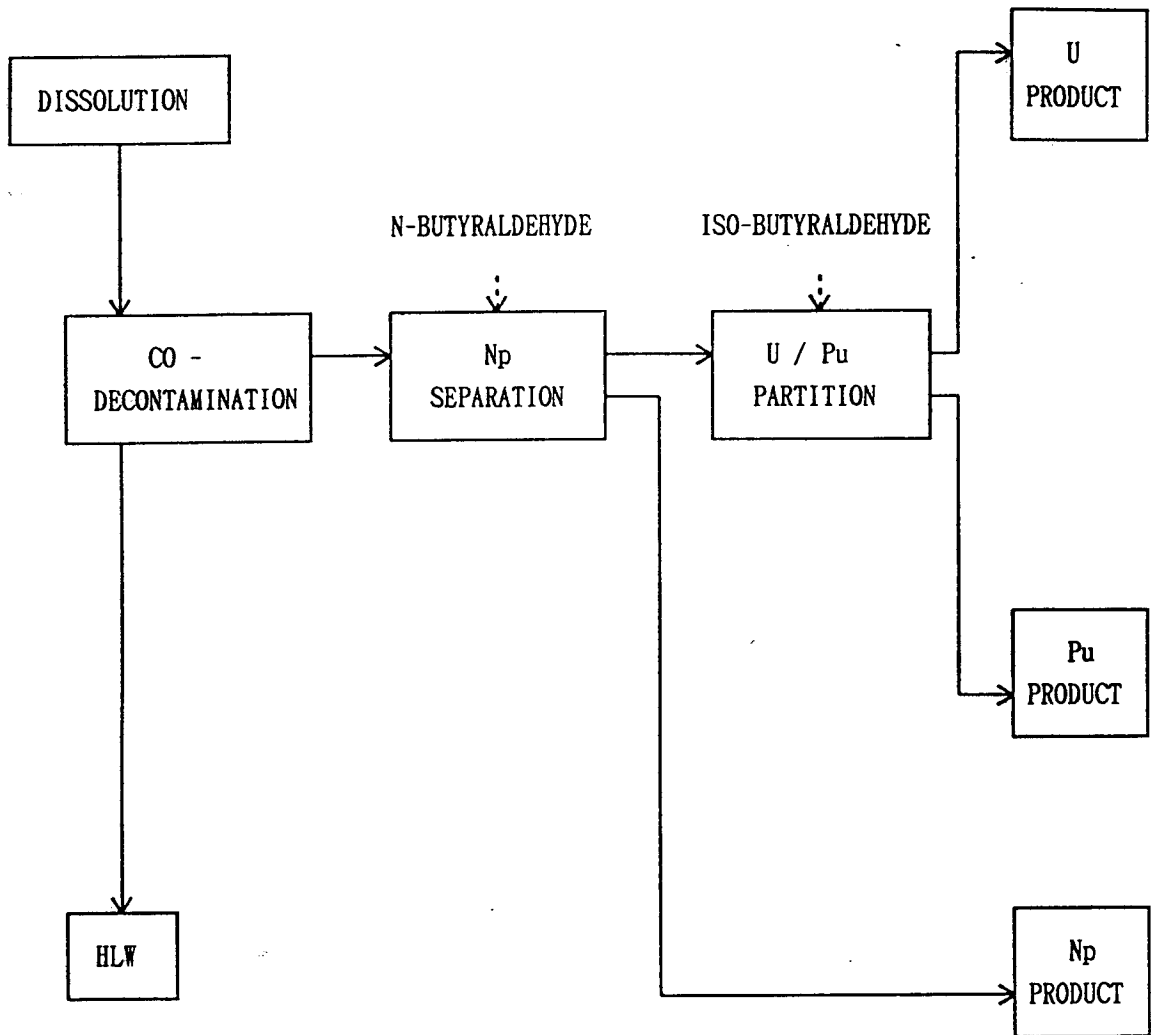


Fig. 3 A proposed flow sheet for Np, Pu and U separation by using normal- and iso-butyraldehydes in the first extraction cycle of reprocessing.

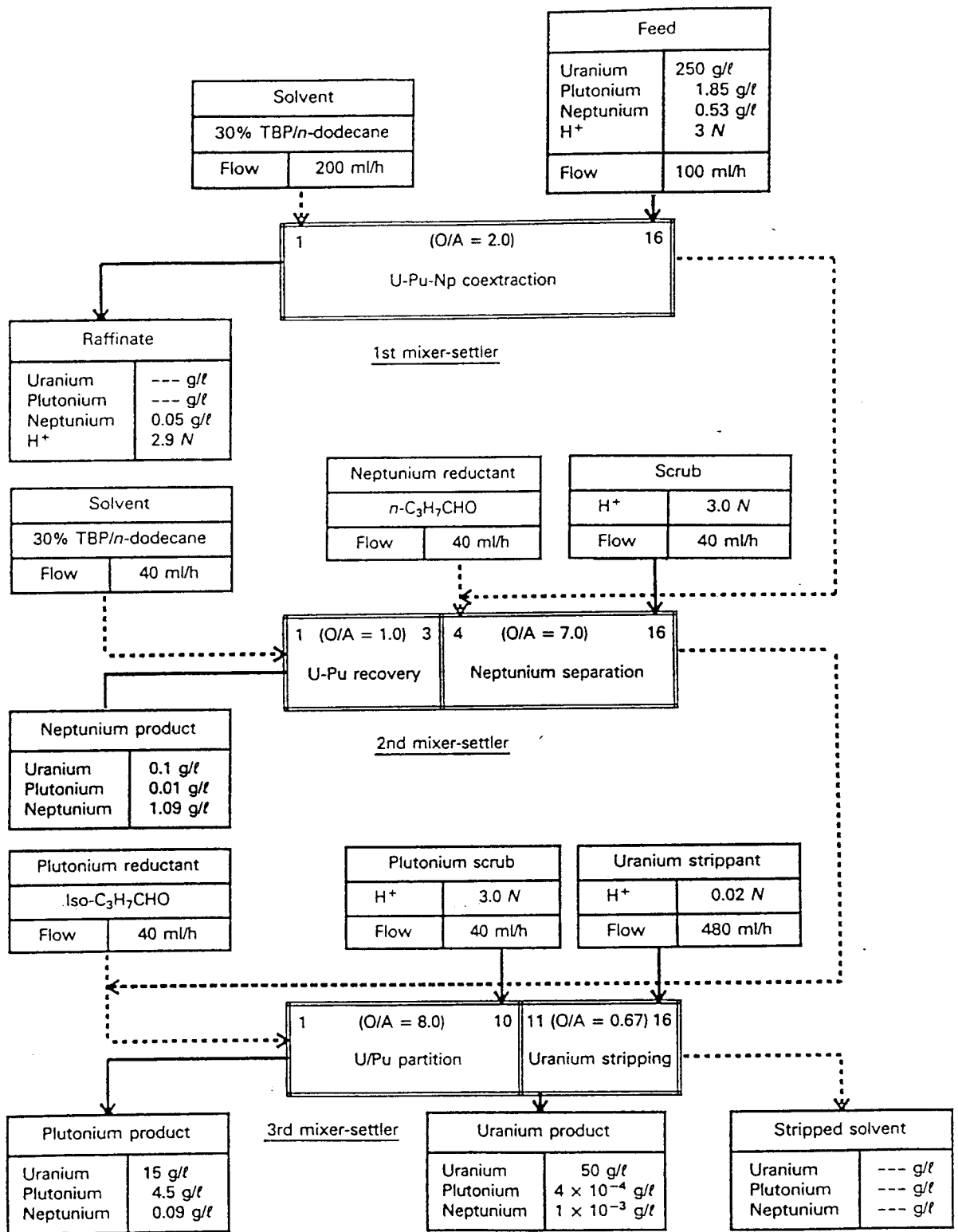


Fig.4 A result of chemical flow sheet study; Concentrations of H⁺, Np, Pu and U in solutions in a flow sheet trial.

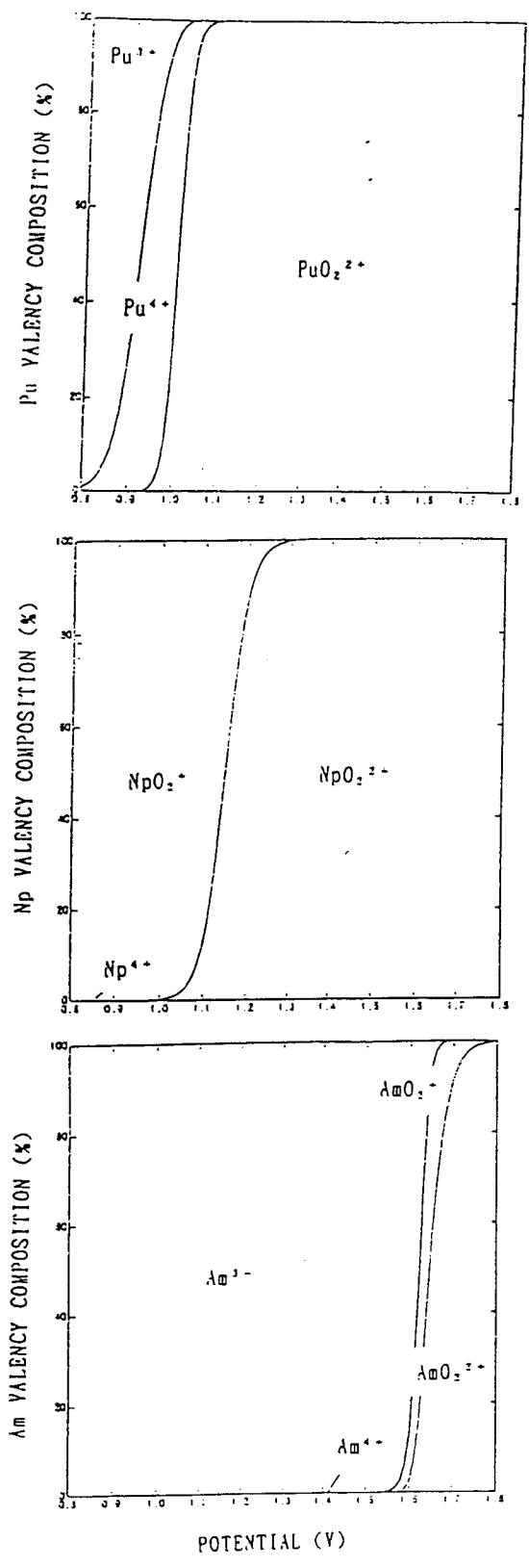
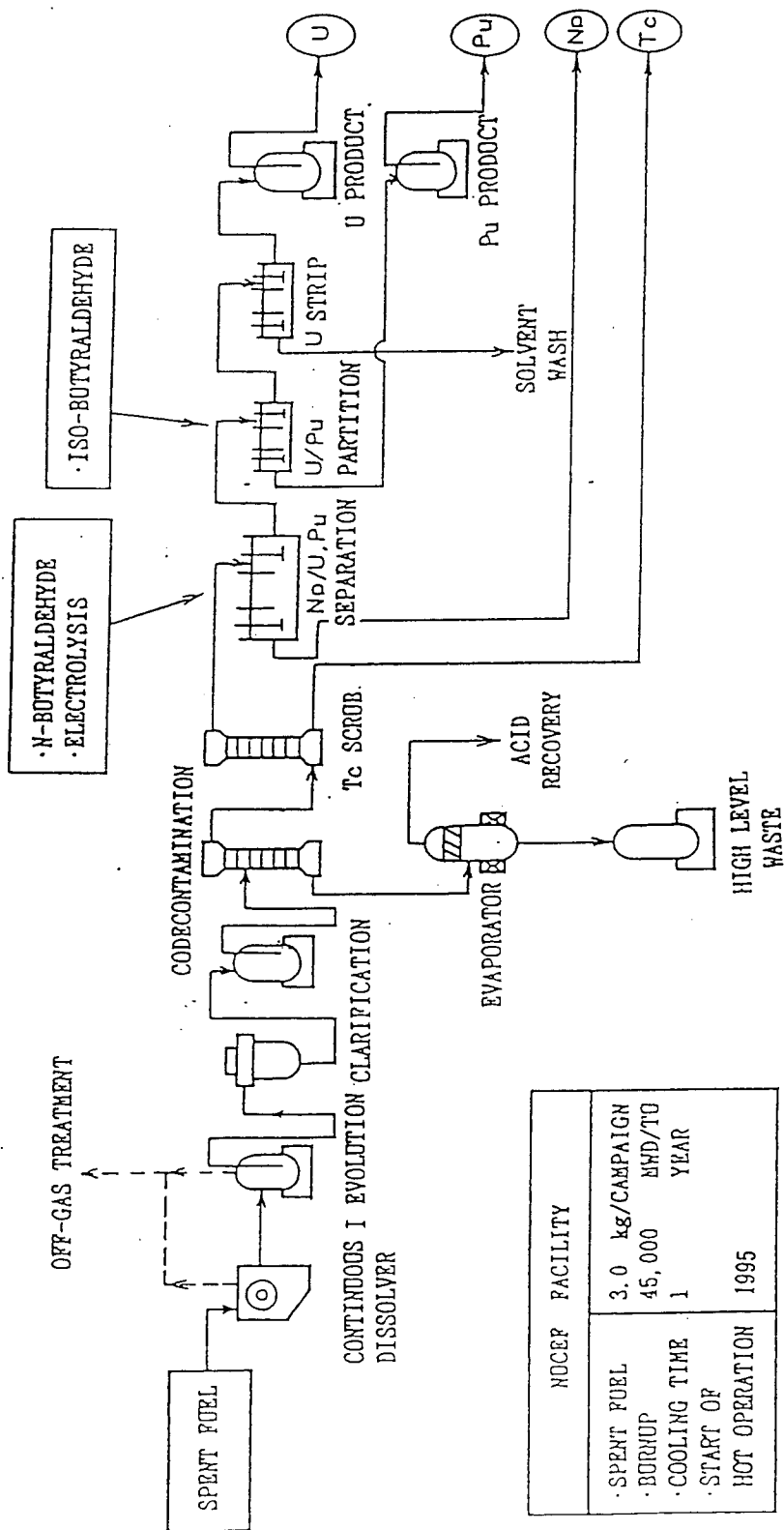


Fig.5 A calculation result of valency composition of actinides



NUCEF FACILITY	
· SPENT FUEL	3.0 kg/CAMPAIGN
· BURNUP	45,000 MWD/TO
· COOLING TIME	1 YEAR
· START OF HOT OPERATION	1995

Fig.6 Main flow sheet of the new bench scale experimental equipment installed in a 7 cell of BECKY facility in NUCEF.

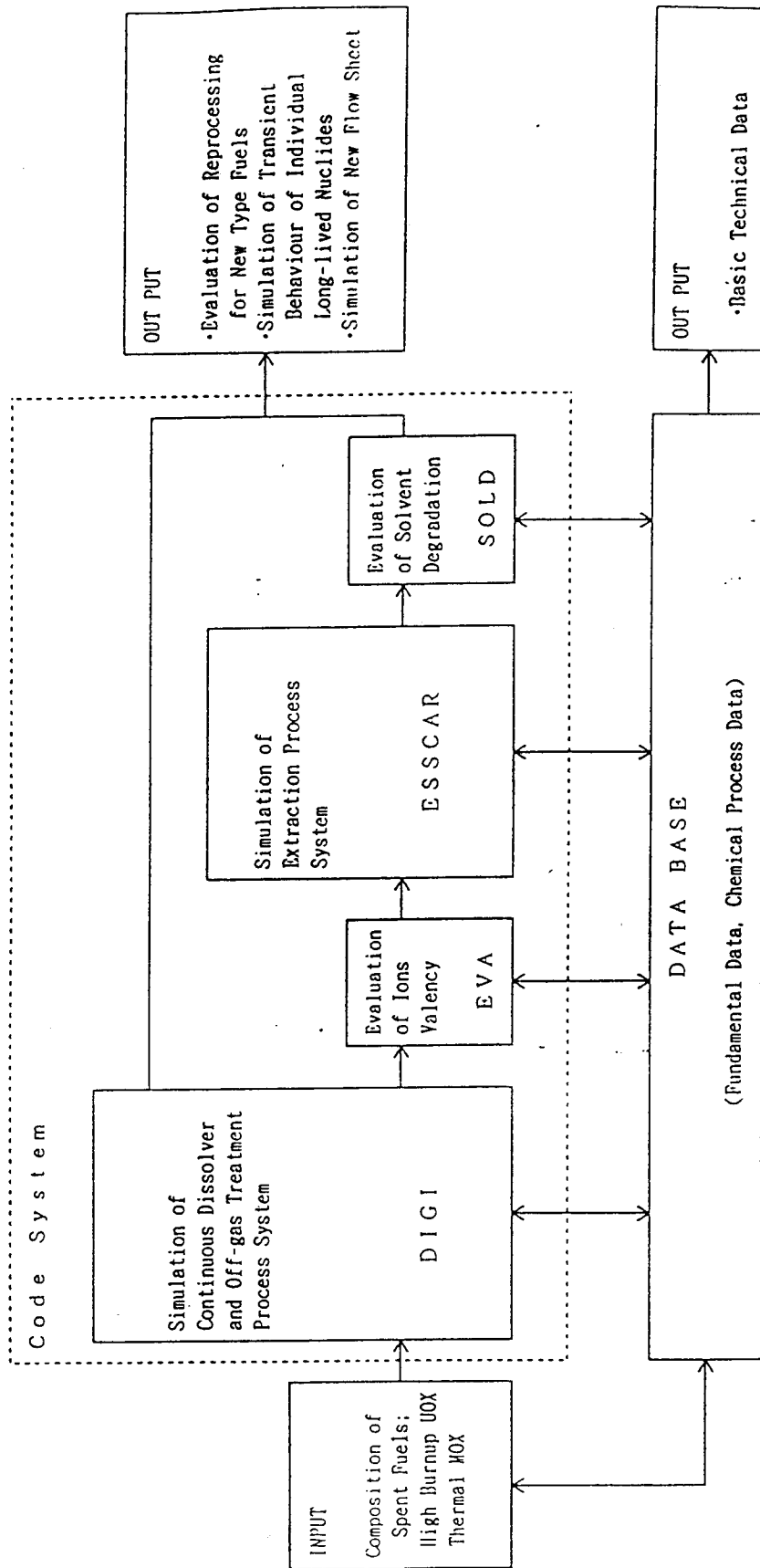


Fig.7 Simulation code system ARECS under development.

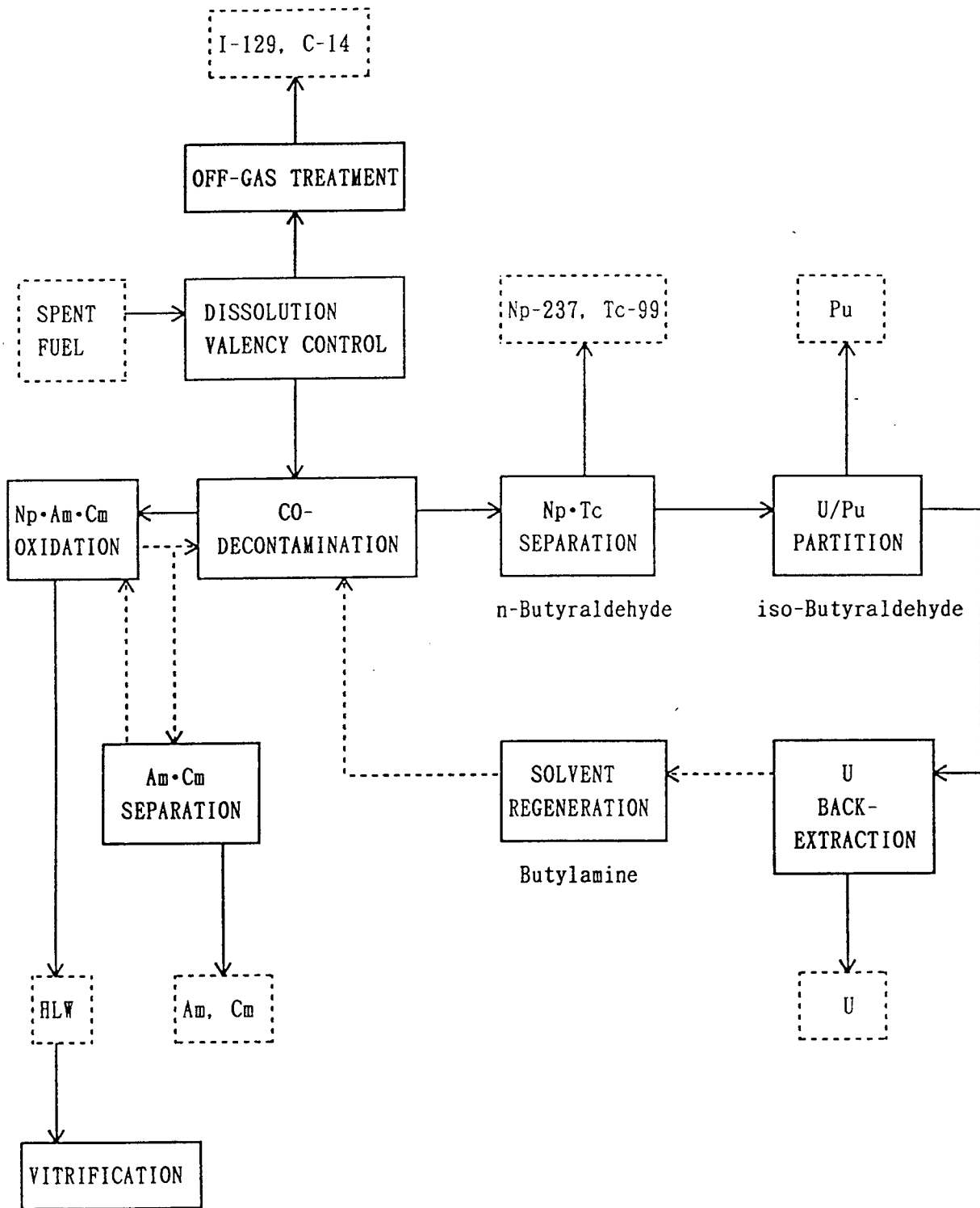


Fig. 8 Block flow diagram of a process concept of the advanced reprocessing incorporated with partitioning; PARC process.