

SESSION 5B

Chairman: Mr. M. HUGON (EC)

RECOVERY OF VALUABLE METALS FROM HIGH-LEVEL RADIOACTIVE WASTE

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Processing steps of the recovery of valuable metals from spent nuclear fuel are studied by means of experiments of lead extraction from high level radioactive waste (HLW) and selective separation of noble metals from simulated waste. Lead extraction and cupellation are found to be effective to recover valuable metals from the actual insoluble residue in dissolver solution of spent fuel. As for refining processes of noble metals extracted in lead, selective separation of ruthenium by ozone oxidation method and mutual separation of rhodium and palladium by solvent extraction method, precipitation method and ion exchange method are examined. These methods are found to have high efficiency for refining these three metals. An optimum conceptual flow sheet for recovery of valuable metals from HLW is derived from these experimental studies.

1. Introduction

Spent nuclear fuels contain significant quantities of valuable metals - the platinum-group metals and technetium. The recovery of the platinum-group metals, palladium, rhodium and ruthenium, leads to a new source of these three metals which have uncertainty in supply because of world's limited producers and are increasing in demand because of the growth of high-technology industry. Spent nuclear fuels also contain technetium which is nearly absent in nature and promising in some kinds of fields of material application. Thus there is considerable incentive to recover the platinum group metals from spent nuclear fuel and various processes to recover them have been evaluated on a laboratory scale[1].

Power Reactor and Nuclear Fuel Development Corporation (PNC) began in 1986 to study and has been developing the technologies to recover and utilize three of the platinum-group metals and technetium from spent nuclear fuel as a part of the partitioning program of HLW (OMEGA project) in cooperation with private companies and universities. All the experimental and bibliographic studies were performed under advice of a special committee - The Technical Committee of Recovery and Utilization of Valuable Metals in Spent Nuclear Fuel sponsored by PNC. The committee had prepared the R&D's program after evaluation of possible flows for recovery and utilization of the valuable metals, which had resulted an optimum flow for the recovery.

Some parts of the platinum-group metals exist as the main constituent of the insoluble residue from dissolution stage of spent fuel in Purex process. The recovery of the platinum-group metals from the insoluble residue is simpler and easier than that from HLLW since the residue consists of metallic alloy containing the metals. Thus we have been developing mainly the processes to recover the noble metals from the insoluble residue.

Fig.1 shows the processing steps for recovery and purification of the platinum-group metals from HLW. In this paper we describe the experimental results on each stage in Fig.1, and discuss a conceptual flow sheet for recovery of the platinum-group metals from HLW.

2. Lead extraction

Lead metal was selected as a scavenger in the first stage of separation of the platinum group metals from other fission products and TRU elements. Sodium borate was used as a glass-forming material to fix other constituents of insoluble residue and calcination.

The actual insoluble residue was obtained from the dissolution stage of FBR spent fuel with burn-up 88000 MWd/t. The majority of particle size of the residue was less than $2\ \mu\text{m}$ in diameter. The residue had the composition of 30% Ru, 7.8% Rh, 8.7% Pd, 12% Tc, 23% Mo, 10% Pu and 2.3% U. The irradiated fuel was dissolved under the mild condition so that some part of plutonium and uranium oxide remained to be undissolved. This enabled to estimate the decontamination factor of TRU elements. The residue of 0.45g was mixed with granular lead metal and sodium borate powder in weight ratio of 50 to 1 and 20 to 1 respectively. Table 1 shows the condition of the lead extraction. The mixture was placed in a mullite crucible and then melted at 800°C for 3hr in the air. Another extraction temperature, 1100°C was used in order to examine influence of temperature on phase separation. After melting the mixture was cooled in the furnace and the lead metal called Pb button was separated from the glass. All the operation of lead extraction test was performed in a hot cell.

The distribution of the platinum-group metals in the Pb button was determined by electron probe microanalysis. Rhodium and lead existed in the Pb button uniformly while ruthenium segregated in the upper part of the Pb button close to the boundary between lead and glass. In some extraction conditions a Pb button was not formed and rather small metal phases were dispersed in the glass. Rhodium and lead seem to be alloy with lead. Technetium existed in the same area where ruthenium segregated in the Pb button. On the other hand, ruthenium, rhodium and palladium were not detected in the glass as if the Pb button formation was not perfect. The volatile fraction of ruthenium was not determined in the hot test, however the cold test gave no indication of volatilization of ruthenium while lead extraction at the same condition.

Radioactivities of the glass as well as the lead were measured to determine the decontamination factors of TRU elements. As shown in Table 1 the decontamination factors for Pu, Am and Cm were more than 200.

3. Cupellation

As the platinum-group metals are contained in a Pb button, Pb separation at early stage may be effective to make the following processes easier. Cupellation method is applied to roughly remove lead from lead-platinum group elements alloy to obtain noble metal bead.

Lead button containing the platinum metals were heated on a magnesia crucible or a calcium phosphate crucible (cupel) at 850-1050°C in the air, and then a metal bead were obtained. The main constituent of the bead was platinum group metals, therefore this method was proved to be available for Pb separation process from Pb button. This treatment is optional and not essential for the following separation processes, so that it possible to dissolve Pb button directly without cupellation.

4. Ruthenium separation

The Pb button, containing the platinum group metals (Ru, Rh, Pd), Tc and Mo, is obtained at the Pb extraction stage as before. After that, the Pb button is dissolved with nitric acid solution and Ru is separated selectively from this solution by ozone oxidation method. Ruthenium is purified by taking advantage of volatility of RuO₄. Ozone gas oxidation process is applied for purification of ruthenium in the sludge from the dissolution treatment. Ozone gas bubbling in nitric acid solution is also effective to remove very small quantity of ruthenium in it. This treatment makes it possible to operate the following processes for mutual separation of rhodium and palladium in a glove box owing to decrease of the activity mainly caused by ¹⁰⁶Ru.

The quaternary Mo-Ru-Rh-Pd alloy was prepared as the simulated insoluble residue based on the method reported by Naito et al. [2]. The composition of the alloy is that of fission produced noble metal alloys and has the ε phase structure. Appropriate amounts of Mo, Ru, Rh and Pd metal powders, all with high purity (99.9%), were mixed and pressed into pellet and then sintered at 1723K in vacuum for 3 hours. The pellets were pulverized to fine powder. The particle size of the powder was adjusted to be 3 μm in average using a vibration mill and a membrane filter.

The Pb metal called Pb button of 5g was separated after the lead extraction of the simulated insoluble residue. The Pb button was dissolved with boiling 3M nitric acid (100ml) for 3 hours, using a flask with a reflux condenser. After dissolution the nitric acid solution was filtrated with a 0.45 μm membrane filter to remove the undissolved powder.

The experimental apparatus employed for Ru separation system is shown diagrammatically in Fig.2. The sample, which was 50mg of the undissolved powder or 50ml of the dissolution fraction after Pb button dissolution process, was transferred to the oxidation reactor at 298K. And then ozone was supplied to the reactor from the reservoir by nitrogen carrier for 4 hours. The operation for the oxidation reaction was repeated 3 times for the undissolved powder and 2 times for the dissolution fraction with every one batch. The chemical compositions of each stage were determined with ICP-AES and ICP-massspectrometry. The distribution of the platinum-group metals in the powder samples was analyzed by electron probe microanalysis.

Fourteen experiments for the undissolved powder were performed and the average value of the results is shown in Fig.3. The recovery of Ru which was converted into RuO₄ and collected in the absorption bottle, was more than 98% in this procedure. Only 2% of Ru was remained in the undissolved powder after the ozone oxidation process. Through this operation nearly all of Rh, Pd and Mo were remained in the undissolved powder and less than 0.1% of those were found respectively in the Ru fraction recovered. The remainder of Ru which is not reacted in this procedure seems to be existed as alloy powder based on the EPMA observation. So a sample for re-extraction with lead was prepared by collecting the remainder of fourteen experiments and a recovery experiment of Ru was performed all over again. The recovery of Ru including a loss due to the lead extraction was higher than 93%. Thus total recovery efficiency of Ru from the undissolved powder was more than 99.8% through the ozone oxidation process coupled with the re-extraction by lead.

The separation of Ru in the solution was also performed by ozone gas bubbling into the dissolution fraction. The recovery of Ru was more than 93% in this procedure. Finally it was found that the transference rate of Ru from the insoluble residue into the dissolution fraction could be decreased less than 1.5×10^{-5} using the ozone oxidation.

5. Mutual separation of rhodium and palladium

Various techniques, which are precipitation, solvent extraction, ion exchange and so on, had been studied or used in the platinum group metals refining industry. Among these techniques, solvent extraction of Pd by amine or sulfide extraction is considered to be promising for Pd separation from the nitric acid solution. Some tests for these extractants, therefore, have been carried out. On the other hand, mutual separation of other elements (Rh, Mo, Pb) by solvent extraction or ion exchange method was considered not to be suitable because a good extractant or an ion exchanger had not been found. On this study, precipitation separation method by adding chemical agents were, therefore, has been studied as refining process of Rh, because Rh is most promising element to be used in common industry.

Tri-n-octylamine (TNOA) is one of amine extractants promising for Pd extraction. The mixture of 10% TNOA and CCl_4 or n-dodecane was used for the present study. Extraction experiments were carried out under the condition of O/A=1 for 30 minutes mixing at room temperature. Distribution ratios are almost coincident whether CCl_4 was used for diluent or n-dodecane, however the third phase formation is observed on either solvent. Dodecyl alcohol (5%) addition to either solvent is enough to prevent formation of third phase, and settling time is rather short (1-2 minutes). Nitric acid concentration dependence on distribution ratios of metals by 10% TOA/n-dodecane extractions is shown in Fig 4. It is seen that distribution ratio of Pb decreases with increasing acidity, and the values are not so high that Pd is extracted effectively at over 3N nitric acid concentration.

Table 2 shows the results of Pd back extraction from 10% TNOA/n-dodecane by various aqueous solutions under the condition of O/A=1 for 5 minutes mixing at room temperature. Palladium is back extracted to 1 wt% thiourea ($\text{CS}(\text{NH}_2)_2$) solution, though it is not done to each other solution. Especially, when ammonia is used, precipitates are formed so that phase separation is difficult. And more than 99% of Pd is stripped by reduction with a hydride solution from the thiourea solution. Chemical form of Pd recovered is powder metal. Thiourea solution, therefore, would be suitable back extraction reagent.

Furthermore the back extraction efficiency was not changed even if thiourea content was changed from 0.1 Wt% to 5wt%. Thiourea is less than 3N nitric acid solution is also available for back extraction and it is useful to promote phase separation, but it is decomposed in 6N nitric acid.

Recently DHS (di-hexyl sulfide) has been studied as a promising extractant of Pd. While most of sulfide extractants are chemically unstable, DHS is rather stable for practical use. Pd extraction study of DHS were hence carried out. Shellsol AB (aromatic solvent) and n-dodecane were selected as diluents. The extraction conditions were those same as TNOA experiments, and DHS content was 10%. Fig.5 shows nitric acid content dependence on distribution ratios of metals by 10% DHS/n-dodecane, which are almost same values as those when shellsol AB is used for a diluent instead of n-dodecane. From this figure, it is seen that the distribution ratios of Pd are extremely high and they are not dependent on nitric acid concentration.

Some reagents for Pd back extraction from 10% DHS/n-dodecane were tested it as TNOA experiments. As shown in table 3, ammonia solution and thiourea solution are effective reagents. To recover Pd from ammonia solution, however, is difficult, though it is easy from thiourea solution by reduction with a hydride solution. Consequently thiourea solution is suitable back extraction reagent from DHS same as TNOA.

Rhodium, Mo and Pb would be contained in the raffinate of Pd extraction process. Neutralization precipitation method was adopted for the Pb separation process. If acetic acid is added to the raffinate before neutralization, Pb would remain in the solution and other elements would be precipitated. This is because Pb acetate is not decomposed by neutralization, though the others are precipitated by hydrolysis with neutralization. pH dependence on the Pb separation was investigated. After adding 20wt% acetic acid, precipitation reaction was executed for 1 hour at room temperature, where pH of the solution was prepared by adding ammonia (<pH10) and sodium hydroxide (pH 10-12). The results are shown in Fig 6. It is seen that more than 90% of Rh and Mo are precipitated as hydroxide at pH8-10 and Mo is dissolved again as molybdate at pH 12, while more than 80% of Pb remains in the solution. More than 99% of Pb is recovered as $\text{Pb}(\text{CO}_3)_2$ from the neutralized solution by adding carbonate to the solution. The chemical form of recovered Pb may be suitable to be returned to the lead extraction process, because $\text{Pb}(\text{CO}_3)_2$ is decomposed easily by heating. The recovery of Pb precipitate would be higher if these procedures are repeated, so that the neutralization method at pH 8-10 would be suitable for Pb separation.

The precipitate recovered on neutralization of the raffinate would contain Rh, Mo and small amount of Pb. As can be seen from Fig.6 mentioned above, more than 80% of Mo is not precipitated in the solution prepared at pH 12 by adding sodium hydroxide but more than 90% of Rh is precipitated. Mutual separation of Rh and Mo, therefore, would be achieved roughly using the precipitation separation method for the precipitate recovered on the Pb separation. As the precipitation separation, it may be appropriate method to dissolve Mo selectively from the precipitate by washing it with ammonia or sodium hydroxide of over pH12. Although Mo is dissolved selectively actually by this method, a small amount of Mo and Pb remain in the Rh precipitate.

Some resin were tested for Rh purification by means of batchwise adsorption. From this test, it is found that chelate resin CS-346 (Sumichelate), amideoxime type, has good performance for Rh purification. The adsorption behavior of CS-346 is shown in Fig.7. It is seen from this figure that Rh would be purified by passing the solution through a column of CS-346 after dissolution of the Rh precipitate with acid solution. On the other hand, coprecipitation method with selenium (Se) or tellurium (Te) was also studied for Rh separation, as this method had been used as analytical method. It was experimentally evaluated that the coprecipitation method was not suitable for practical process because of its long reaction time.

The results presented above indicate that a flow sheet shown in Fig.8 is desirable for a mutual separation process of palladium and rhodium in nitric acid solution. The starting solution of this process flow is the nitric acid solution containing Pb, Pd, Rh and Mo. Palladium is separated selectively from the solution using DHS extraction process, and it is back extracted to thiourea solution, so that it is recovered as metal by reduction agents. On the other hand, the raffinate is added with acetic acid and ammonia solution, so that Pb is recovered to be returned to the former process. The precipitate is treated with sodium hydroxide solution to be separated to Mo and Rh fractions. Rh would be refined finally using chelate resin.

6. Conceptual flow sheet

Based on the results described above, the flow sheet for recovery of noble metals from HLW has been established, that is shown in Fig.9. Lead extraction method is chosen for the first step to separate the noble metals from other fission products because of compatibility with vitrification of HLLW for geologic disposal. After the lead extraction, the cupellation method is applied to roughly remove lead from lead-platinum group elements alloy to obtain noble metal bead. Then the bead is dissolved in nitric acid. Ruthenium in the bead is almost not dissolved in nitric acid, therefore sludge mainly containing ruthenium is separated by filtration. After the separation of ruthenium, aqueous processes are applied for mutual separation of rhodium and palladium.

7. Conclusion

We have determined the conceptual flow sheet as for platinum group metals containing in the insoluble residue. Each separation method used in the flow sheet shown in Fig.9 has high separation factor enough for practical use. It is required to perform the recovery steps continuously and determine the final recovery efficiencies of platinum group metals in order to confirm the effectivity of the flow sheet. The objective of this study is to establish a flow sheet for recovery of the valuable metals from HLW. We are planning to modify the flow sheet for recovery of other valuable metals, especially technetium.

References

- [1] G.A.Jensen, A.M.Platt, G.B.Mellinger and W.J.Bjorklund, Nucl.Technol.,65, 305 (1984).
- [2] K.Naito, T.Matsui, H.Nakahira, M.Kitagawa and H.Okada, J. Nucl. Mater., 184, 30(1991).

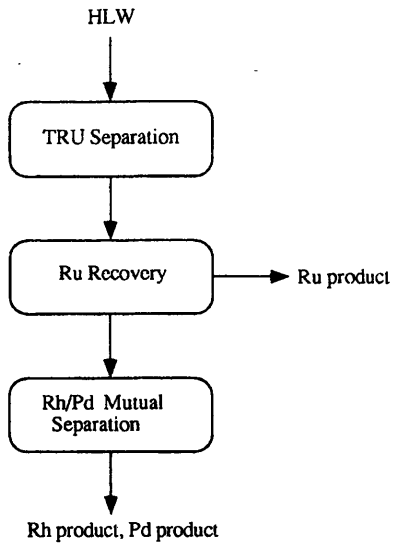


Table 1 Decontamination factors of lead extraction for some TRU nuclides

Nuclide	Activity in Lead (A) [kBq/g]	Activity in Glass (B) [kBq/g]	DF (B/A)
$^{239}\text{Pu} + ^{240}\text{Pu}$	1.1×10^2	1.5×10^{-3}	140
^{241}Am	2.0×10^2	5.9×10^{-4}	300
^{242}Cm	5.1	1.2×10^{-3}	240
^{244}Cm	1.7×10^2	4.4×10^{-4}	260

Fig.1 Processing steps for recovery and purification of the platinum group metals from HLW

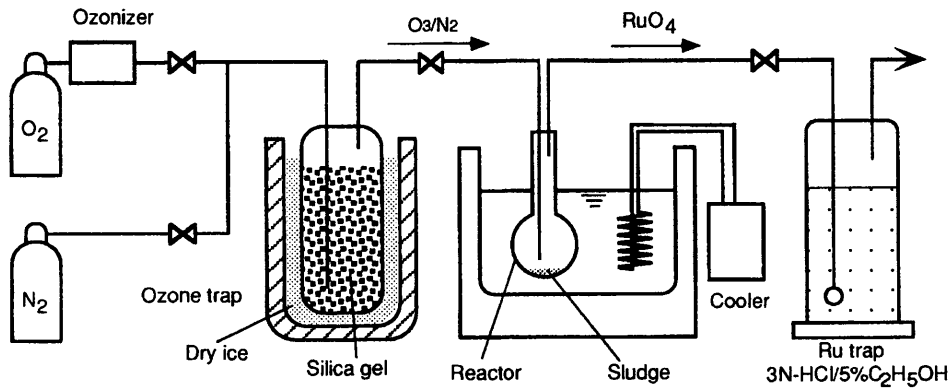


Fig.2 Apparatus for ruthenium oxidation recovery

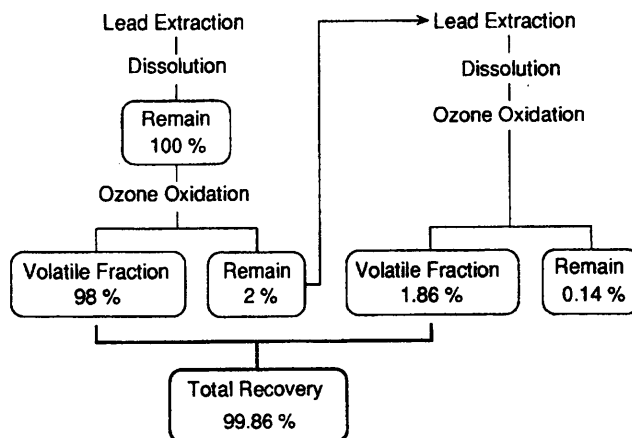


Fig.3 Total efficiency of Ru recovery by ozone oxidation method

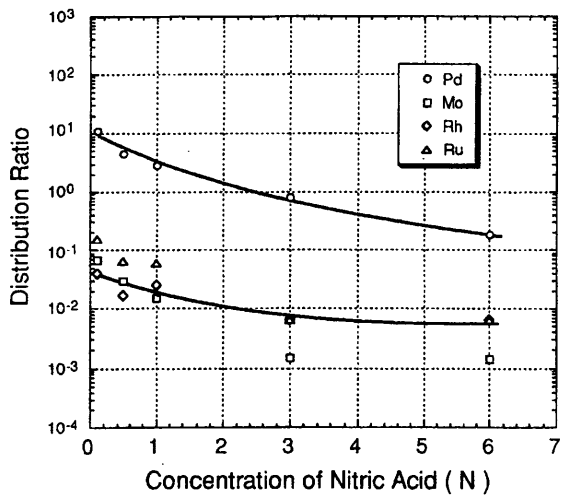


Fig.4 Distribution ratios of metals by 10%TNOA in n-dodecane as a function of nitric acid concentration

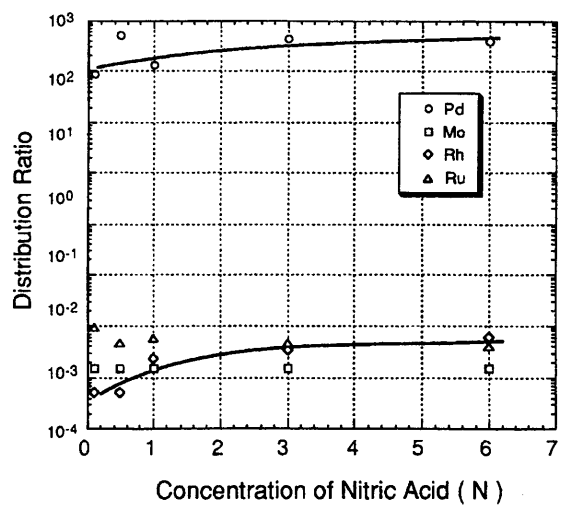


Fig.5 Distribution ratios of metals by 10%DHS in n-dodecane as a function of nitric acid concentration

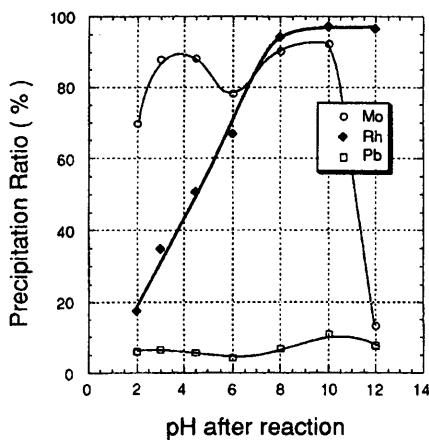


Fig.6 Lead separation from metals precipitate rate of Pb, Rh, Mo as a function of pH by precipitation method (neutralization)

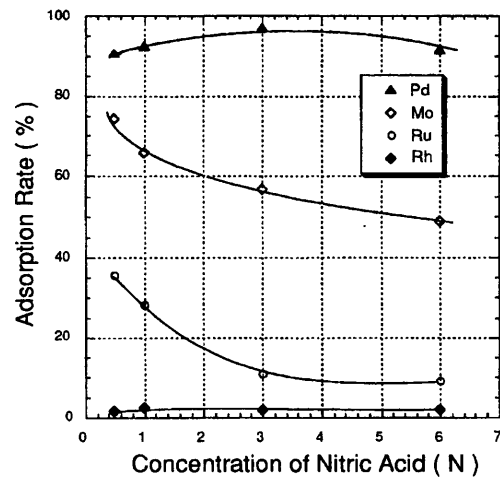


Fig.7 Adsorption rate of metals as a function of nitric acid concentration by chelata resin CS-346

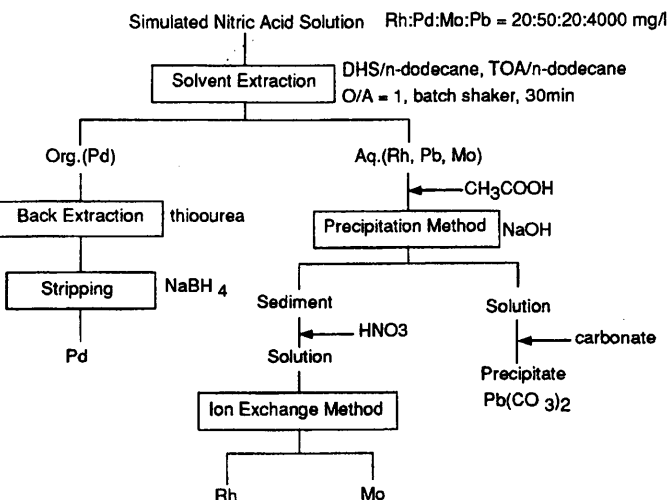


Fig.8 Flow sheet for mutual separation of platinum group metals

Table 2 Palladium back extraction from TNOA/n-dodecane by various aqueous solution

Back Extraction Agent	Back Extraction Rate (%)
Acid	
0.1N HNO ₃	7
6.0N HNO ₃	25
0.1N HClO ₄	26
3.0N HClO ₄	18
Alkali	
6.0M NH ₄ OH	>99
0.5M NaOH	8
4.0M NaOH	23
0.5M Na ₂ CO ₃	2
Others	
1.0wt% (NaH ₂)CS	>99
20wt% Na ₂ S ₂ O ₃	86

Table 3 Palladium back extraction from DHS/n-dodecane by various aqueous solution

Back Extraction Agent	Back Extraction Rate (%)
Acid	
0.1N HNO ₃	N.D.
6.0N HNO ₃	N.D.
0.1N HClO ₄	N.D.
3.0N HClO ₄	N.D.
Alkali	
6.0M NH ₄ OH	>99
0.5M NaOH	9
4.0M NaOH	25
0.5M Na ₂ CO ₃	27
Others	
1.0wt% (NaH ₂)CS	>99
20wt% Na ₂ S ₂ O ₃	73

N.D. : not detected

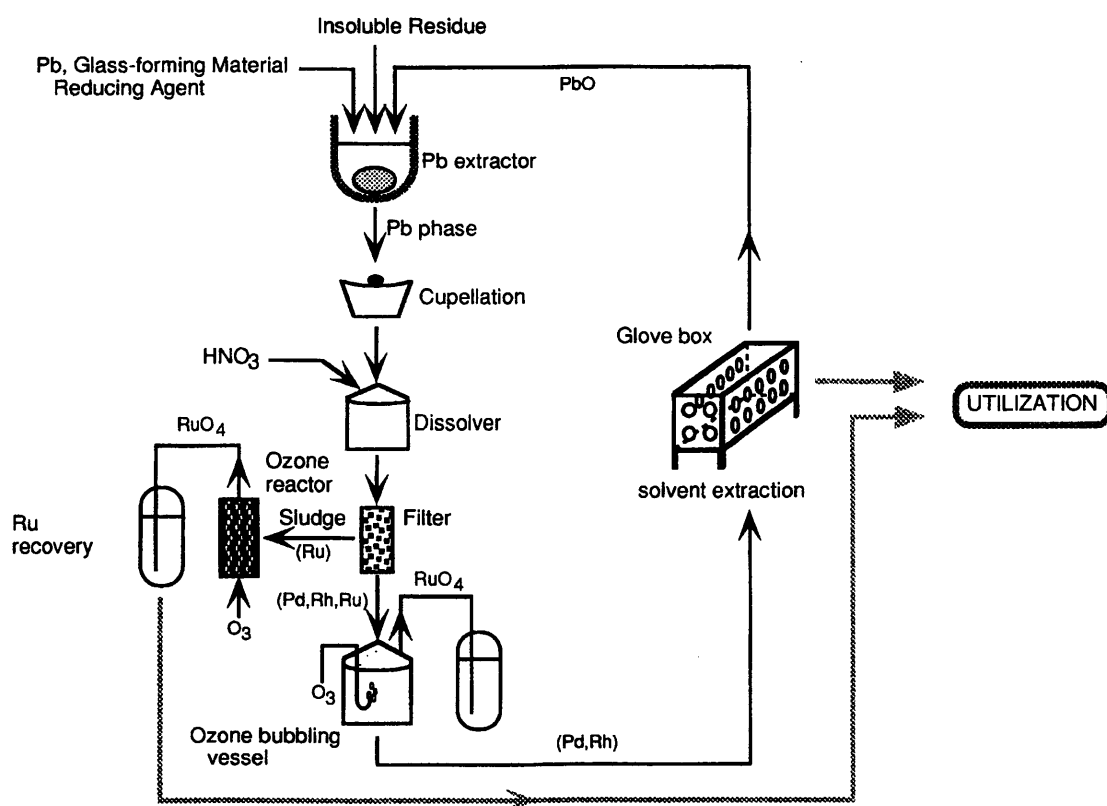


Fig.9 Conceptual flow sheet for recovery of noble metals from insoluble residue

PARTITIONING TEST FACILITY CONSTRUCTED IN NUCEF

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Partitioning Test Facility was constructed in NUCEF (Nuclear Fuel Cycle Safety Engineering Research Facility) at JAERI, Tokai, in order to demonstrate the 4-group partitioning process developed in JAERI using real high-level liquid waste (HLLW). The present paper shows the purpose of the facility, the equipments in the facility and the preliminary results of the partitioning tests with simulated HLLW.

In the partitioning facility, 2 to 20 L of HLLW (5000 Ci at maximum) can be treated per experiment. Main components in the facility are a vessel for denitration, a filter unit, extractors (two 16-stage mixer-settler units), adsorption columns and the related equipments.

Partitioning tests with simulated HLLW are now in progress. The results will be compared with those of the tests with real HLLW. In the latest test, lanthanides were almost completely extracted with DIDPA and well back-extracted with 4 M HNO_3 .

1. Purpose of the facility

The main purpose of the facility is to demonstrate the 4-group partitioning process developed in JAERI using real high-level liquid waste (HLLW). The results of the partitioning tests with real HLLW are compared with those of the tests with simulated HLLW. The comparison and the further examination on the properties of real HLLW and on the influence of radiation would give validity and limitation of the experiments with simulated HLLW, which have been carried out before and will be performed in the future from the viewpoints of basic chemistry and chemical engineering.

The facility will be used also for the test of the optimized or advanced process and a new partitioning process to which new extractants, new adsorbents and new methods are applied. The facility has enough flexibility.

2. The 4-group partitioning process

The flow scheme of the 4-group partitioning process is shown in Fig. 1. In this process, elements in HLLW are separated into four groups: transuranium elements (TRU), Tc - platinum group metals (PGM), Sr - Cs and the other elements. For the TRU separation, extraction with diisodecylphosphoric acid (DIDPA) has been studied. One of the extraction process established is shown in Fig. 2, which includes the separation of Am, Cm from lanthanides by selective stripping with diethylenetriaminepentaacetic acid (DTPA). For the separation of Tc and PGM, two methods were studied; one is the precipitation by denitration and the other is the adsorption with active carbon. An adsorption method with inorganic ion exchangers (titanic acid and zeolite) was developed for the separation of Sr and Cs.

3. Outline of the facility

In the partitioning facility, 2 to 20 L of HLLW (5000 Ci at maximum) can be treated per experiment. The reprocessing facility, which was installed in the same hot cell in NUCEF, will provide real HLLW. The partitioning facility can also accept HLLW from other reprocessing plants.

Main components in the facility are Denitration and Concentration Vessel, Filter Unit, Extractors, Adsorption Columns and the related equipments. In the Denitration and Concentration Vessel, 6 L of HLLW can be concentrated and 2 - 3 L of HLLW can be denitrated. Precipitates formed in this vessel are separated by sintered-metal filter in the Filter Unit. Two 16-stage mixer-settler units are installed for the separation of TRU from HLLW. The process to be tested with these extractor units is composed of the following three steps: extraction with DIDPA, back-extraction with 4 M HNO₃ and back-extraction with H₂C₂O₄, steps surrounded by broken lines in Fig. 2. Other steps of extraction and back-extraction can also be tested by changing the reagents and by changing the mixer-settlers if required. Particularly, the separation of Am, Cm from lanthanides by selective stripping with DTPA is one of the most important items to be tested in the future. The Adsorption Columns can be used in two adsorption processes; one is adsorption of Tc and PGM with active carbon and the other is adsorption of Sr and Cs with inorganic ion exchangers. Precipitation of Tc and PGM by denitration is also examined using the Denitration and Concentration Vessel.

The flow sheet of the partitioning test facility is shown in Fig. 3. The facility is also equipped with a vessel for oxalate precipitation.

4. Partitioning tests with simulated HLLW

Partitioning tests with simulated HLLW are now in progress. The results will be compared with those of the tests with real HLLW, as mentioned above. The tests with simulated HLLW showed that all the components in the facility could be operated safely and remotely.

In the latest test, phosphoric acid was added to HLLW before denitration as pre-treatment for the DIDPA extraction in order to completely remove Zr, which sometimes disturbs the DIDPA extraction. About 99.5 % of Zr were removed from the simulated HLLW as a precipitate in this pre-treatment step. In the DIDPA extraction step, lanthanides were almost completely extracted with DIDPA and well back-extracted with 4 M HNO₃. Table 1 shows fractional distribution of each element. The ratio of Nd extracted was more than 99.99 %. Since the extraction behavior of Am is very similar to that of Nd, Am would also be extracted with the high yield in this step. The back-extraction of lanthanides was not complete but would be improved by

adding one more stage (presently 5 stages) and/or by raising temperature. Other elements except Fe were not extracted and therefore well separated from lanthanides. Fe was stripped from the solvent in the second back-extraction step with $H_2C_2O_4$ with a yield of 99.8 %.

Element behavior at the following steps in the 4-group partitioning process will be investigated in the next test.

5. Future plan

In 1996 - 97, tests with some tracers (^{237}Np , ^{99}Tc , etc.) in simulated HLLW will be performed to examine the behaviors of the elements that are not contained in the simulated HLLW. Partitioning tests with real HLLW are scheduled in 1998. The separation of Am and Cm from lanthanides will be included in the test with real HLLW. Further, the facility will be used for the test of a new partitioning process with real HLLW.

Table 1 The fractional distribution (%) of each element at the DIDPA extraction step in the partitioning test with simulated HLLW at NUCEF.

Element	Raffinate	Back-extracted with 4M HNO_3	Solvent
Y	< 0.002	5.6	94.4
La	< 0.06	> 99.93	< 0.01
Nd	< 0.01	98.7	1.3
Gd	< 0.04	97.5	2.5
Fe	4.64	0.52	94.84
Ru	98.7	0.2	1.1
Rh	> 99.0	0.9	< 0.1
Pd	98.2	0.8	1.0
Sr	> 99.98	0.02	< 0.001
Ba	> 99.99	0.01	< 0.001
Rb	> 99.96	< 0.03	< 0.01
Cs	> 99.90	< 0.07	< 0.03

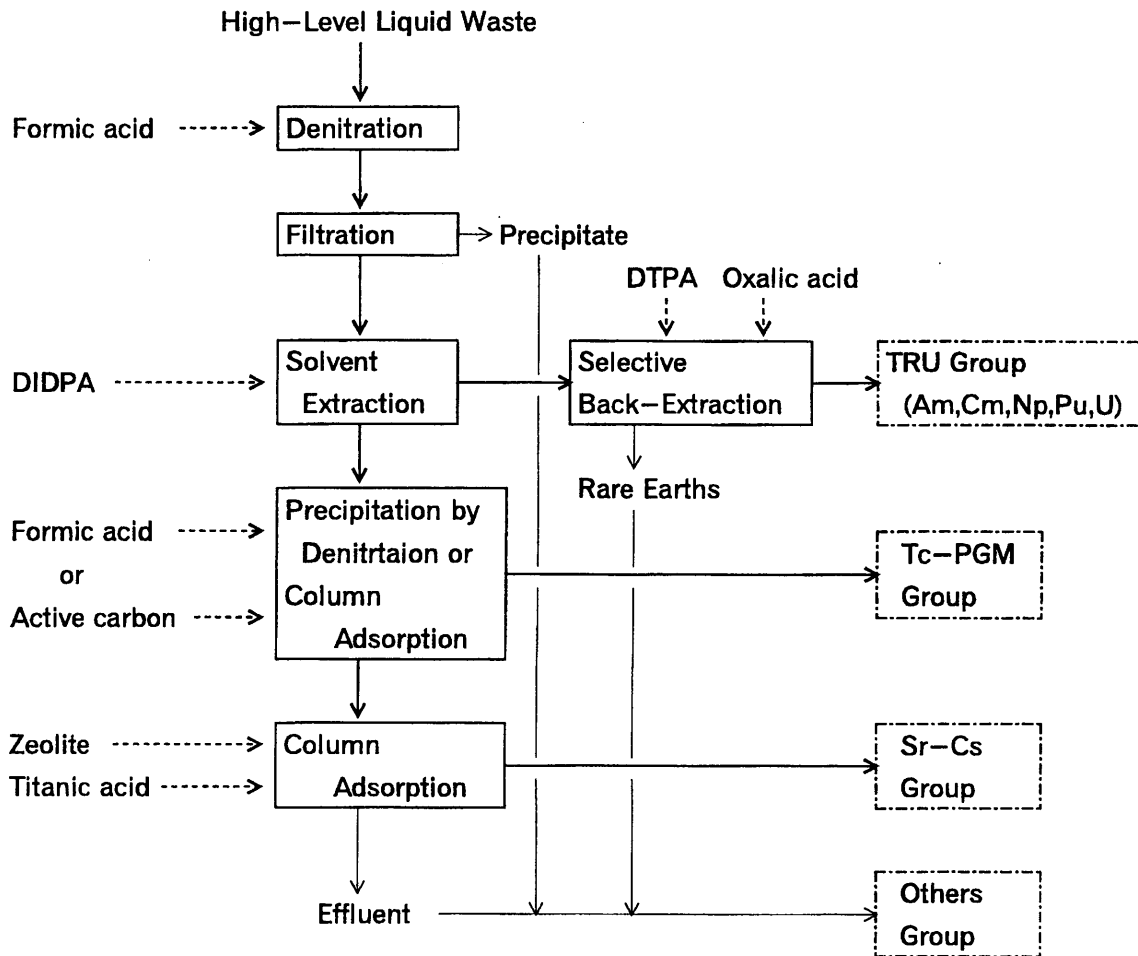


Fig. 1 The 4-Group Partitioning Process to be tested in NUCEF using real high-level liquid waste

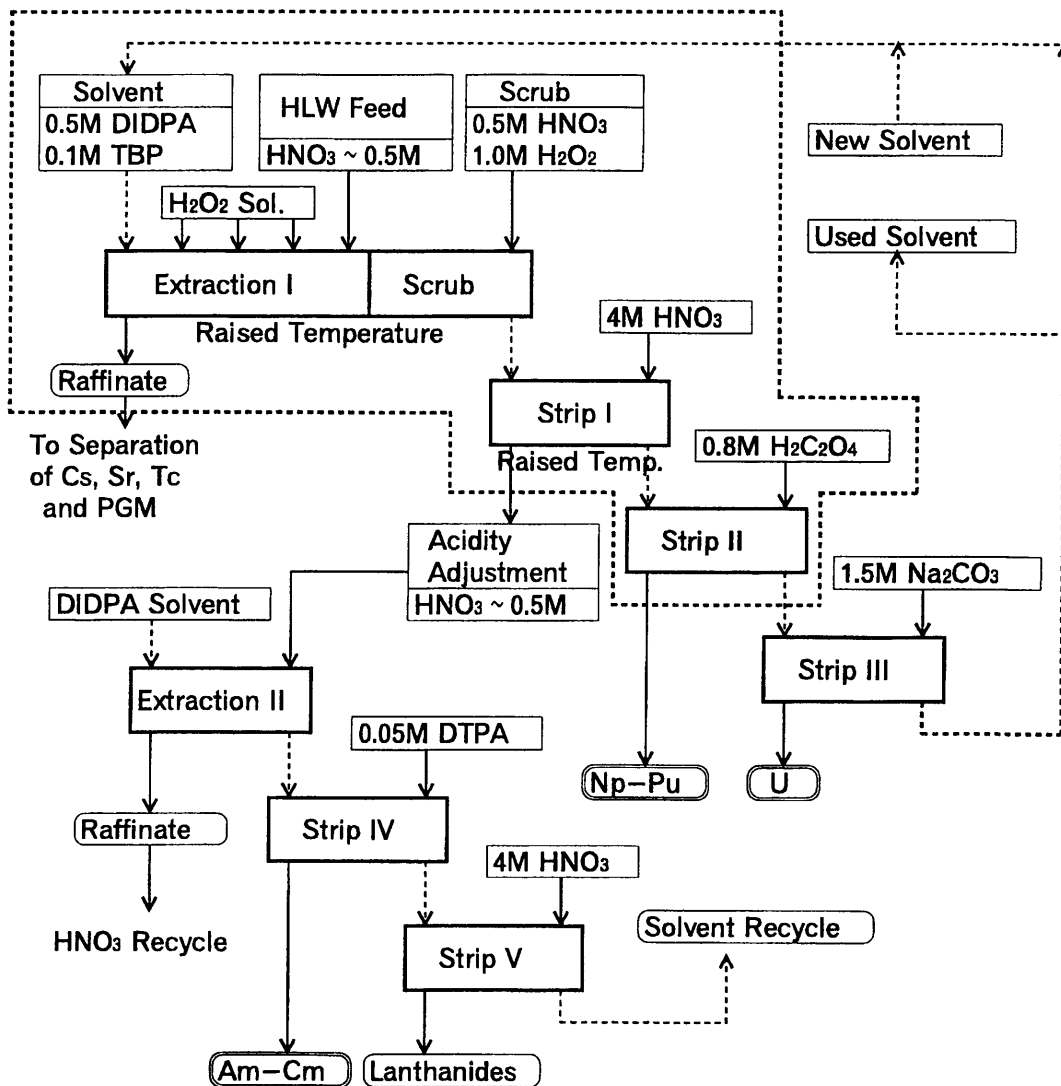


Fig. 2 DIDPA Extraction Process including the Separation of Am and Cm from Lanthanides. - Two-Cycle Process -

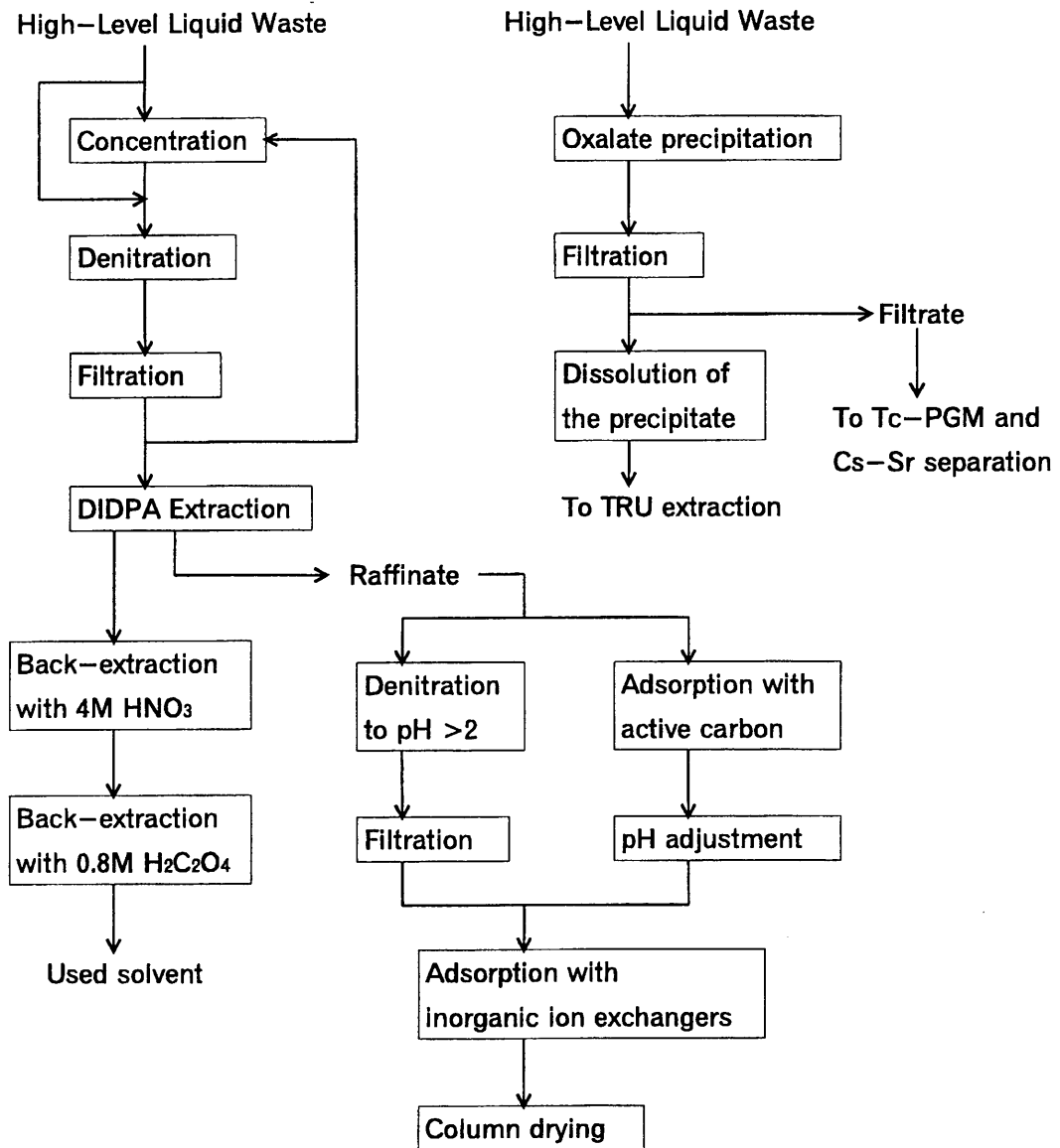


Fig.3 Flow Sheet of the Partitioning Test Facility in NUCEF

ENHANCEMENT OF CONFINEMENT CAPABILITY OF LONG-LIVED NUCLIDES
IN A SIMPLIFIED FUEL CYCLE

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ABSTRACT

Study on PARC(Partitioning Conundrum Key) process concept is under way using Back-End Cycle Key Elements Research Facility(BECKY) in NUCEF. Reprocessing should be performed economically and safely. Process simplification will be effective to improve economical competitiveness. And enhancement of confinement capability of long-lived nuclides will be effective to improve the safety standard and to ease the people's anxiety about reprocessing wastes. Those two measures are apparently contradictory each other. However, both measures are closely linked and interdependent in some cases. We are studying simplified reprocessing concept PARC which is expected to reduce risks due to long-lived nuclides in the reprocessing waste management, not only in the geological disposal but also in the environmental releases.

1. Introduction

It is important that the application of separation and transmutation functions of long-lived nuclides does not pose a substantial increase of economical burden on actual nuclear fuel cycle. According to the study until now, neptunium(Np-237), technetium(Tc-99), plutonium, americium and iodine(I-129) are assessed to take relatively significant role on potential hazard as long-lived elements in HLW.

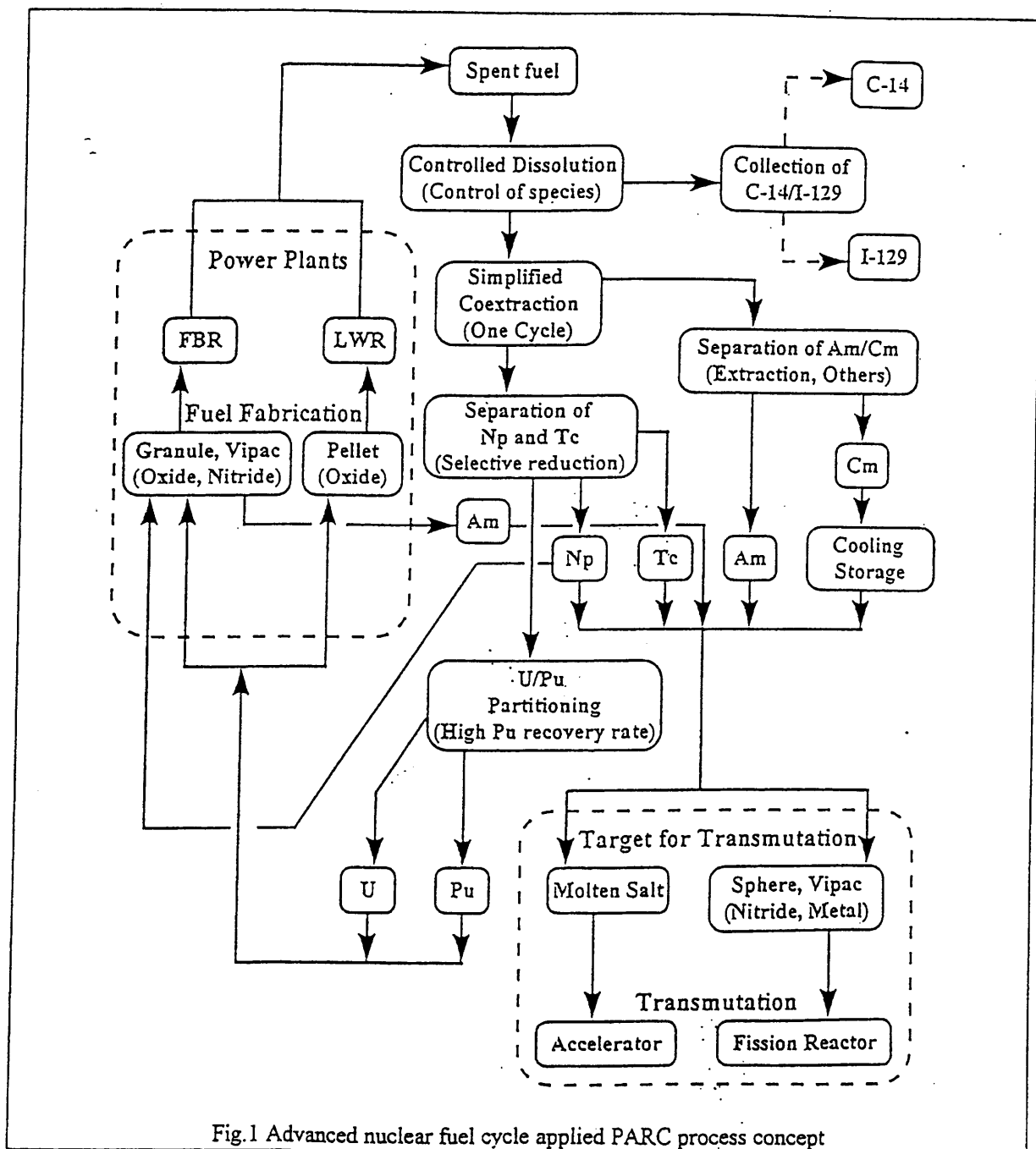


Fig.1 Advanced nuclear fuel cycle applied PARC process concept

Np and Tc are special elements which easily diffuse into products in reprocessing and migrate fast in geological matrix, too. This characteristic property makes those elements assessed as highly potentially

hazardous. Although Pu and the daughter Am do not migrate fast in geological matrix, the influences of these elements are estimated to be significant because of the increased amount recycled in the future fuel cycle. I-129 and C-14, the latter has been assessed from long ago to have a significant influence on the public health⁽¹⁾, are volatile and easy to be released into the environment. Those nuclides, alike Kr-85, are assessed to be relatively influential on the effective dose of inhabitants near reprocessing facility. Technologies for economical and effective separation of the above-mentioned long-lived nuclides are expected to be useful for enhancement of radioactivity confinement capability in reprocessing. Particularly, enhancement of separation efficiency for the elements which are susceptible of diffusing into products, such as Np and Tc, improves the performance of separation step. From these points of view, we are studying PARC concept of reprocessing incorporated with transmutation function of long-lived nuclides. Figure 1 shows our concept of fuel cycle in the future.

2. Back-End Cycle Key Elements Research Facility BECKY for Chemical Process Study

A research facility, NUCEF-BECKY, has been utilized in JAERI at 1995 to study nuclide behaviors in chemical processes and to study feasibility of advanced processes. Miniature scale experimental equipment has been installed in a small-scale $\alpha \gamma$ cell of BECKY with a capacity of 3kg/y of highly radioactive spent fuel. Main flow sheet of equipment for reprocessing study is shown in Fig.2.

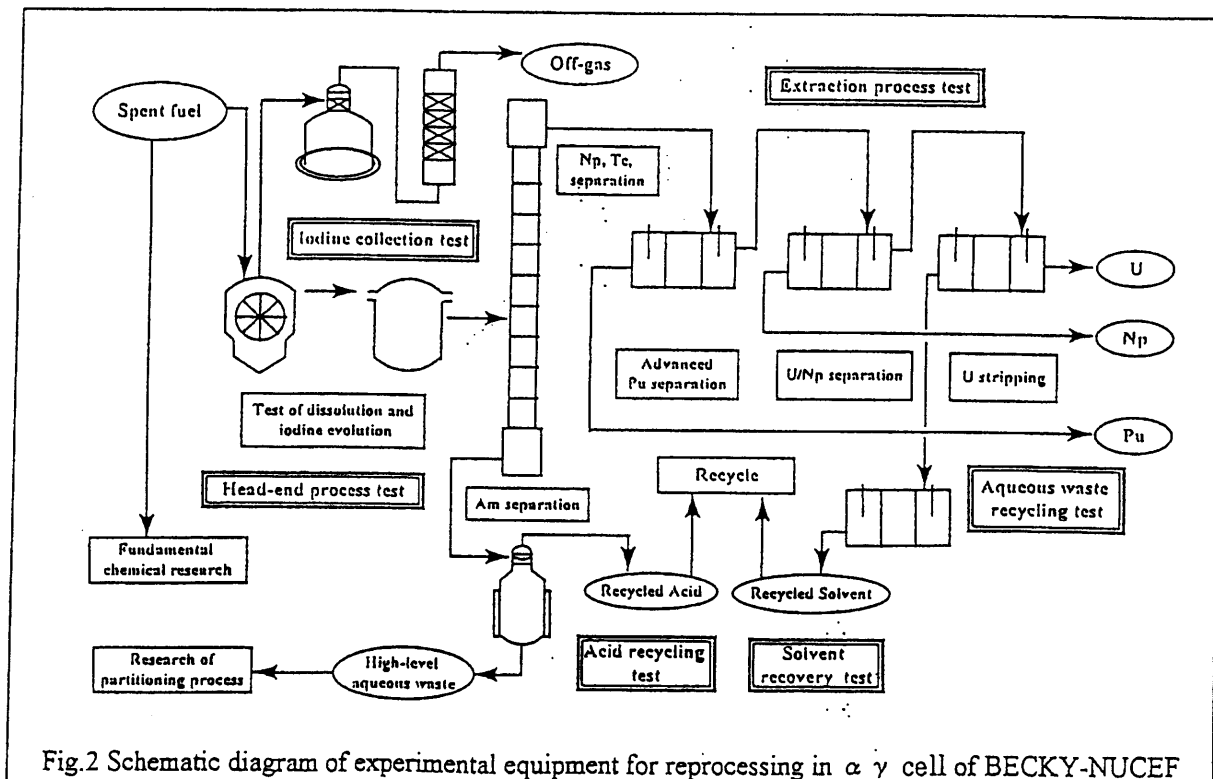


Fig.2 Schematic diagram of experimental equipment for reprocessing in $\alpha \gamma$ cell of BECKY-NUCEF

Experiments started with uranium mixed with simulated fission products for preparing actual hot test

with spent fuel around 1997. Data of dissolution, iodine distribution and extraction have been collected so far. Distribution profiles of iodine in the head-end process were measured using I-131 as a radioactive tracer. Concentration of nitrous acid were measured in continuous dissolver and pulsed columns. Chemical process study program consists of five subjects: (1) Kinetics study of spent fuel dissolution, (2) Feasibility of simplified extraction process, which separates Np and Tc as well as U and Pu, (3) Assessment of capability of minor radioactive nuclides confinement in the process, (4) Development and verification of process simulation code. (5) Adsorption technique of iodine and carbon-14 from dissolver off-gas.

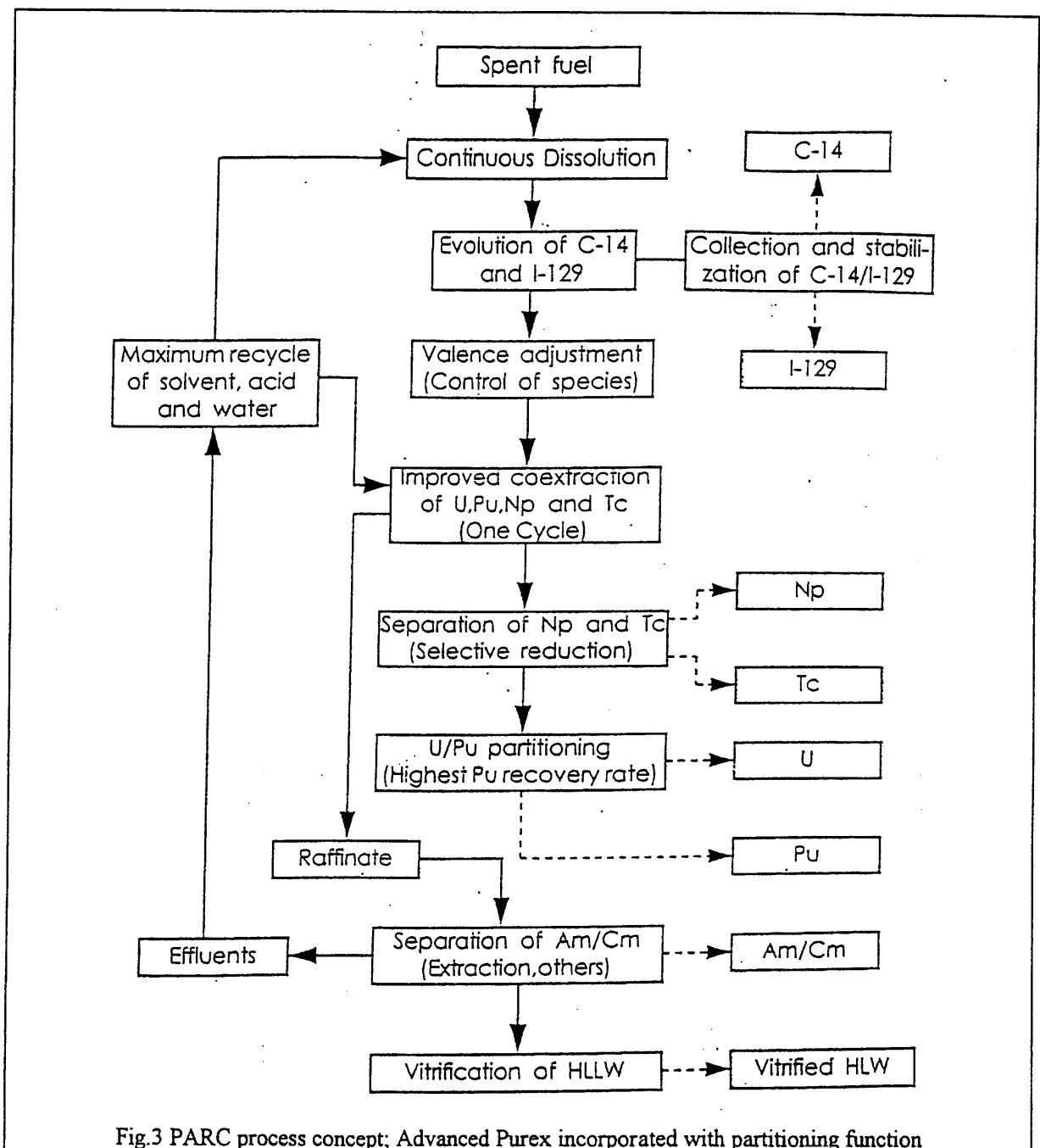
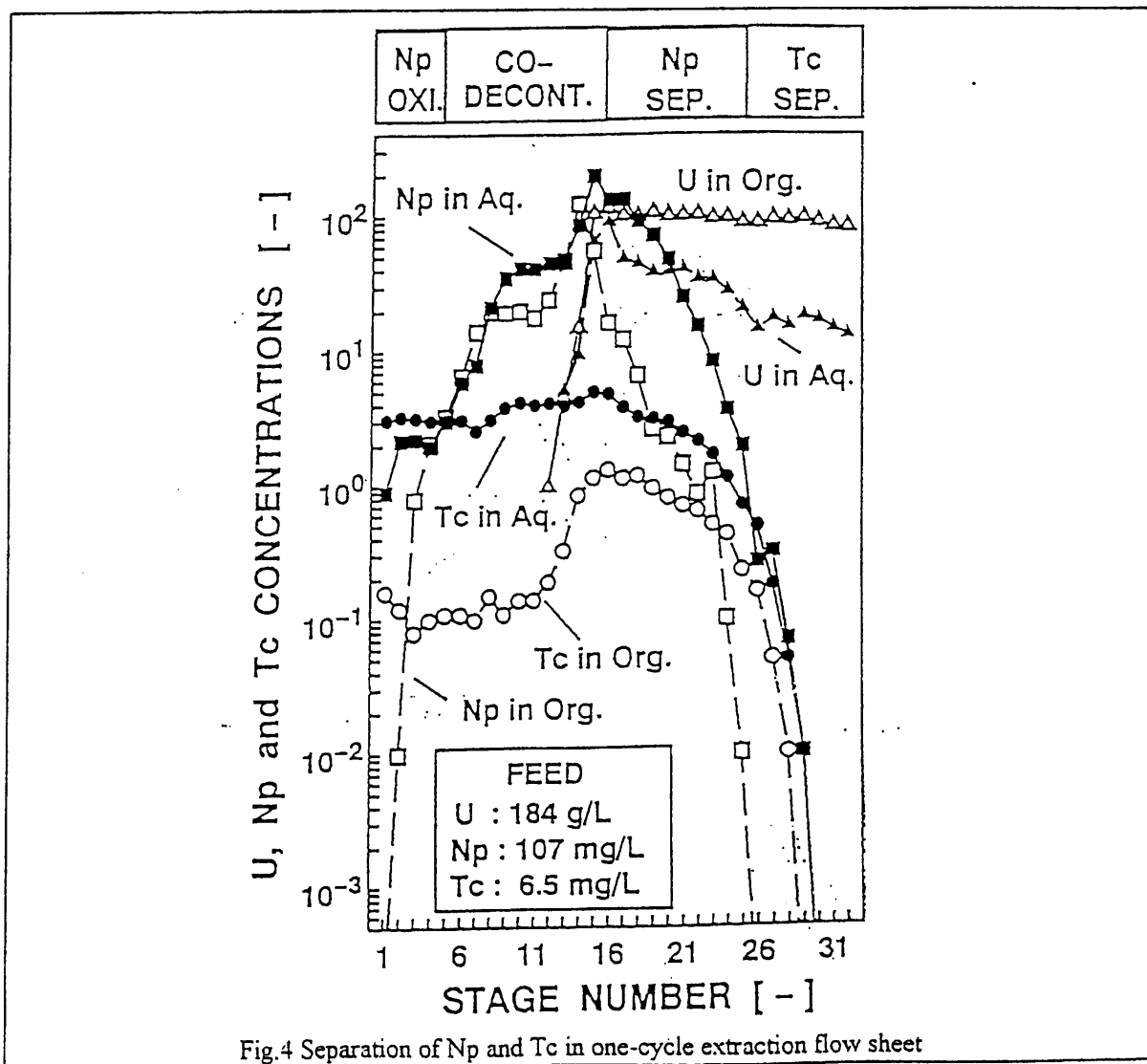


Fig.3 PARC process concept; Advanced Purex incorporated with partitioning function

3. Simplified Chemical Processing

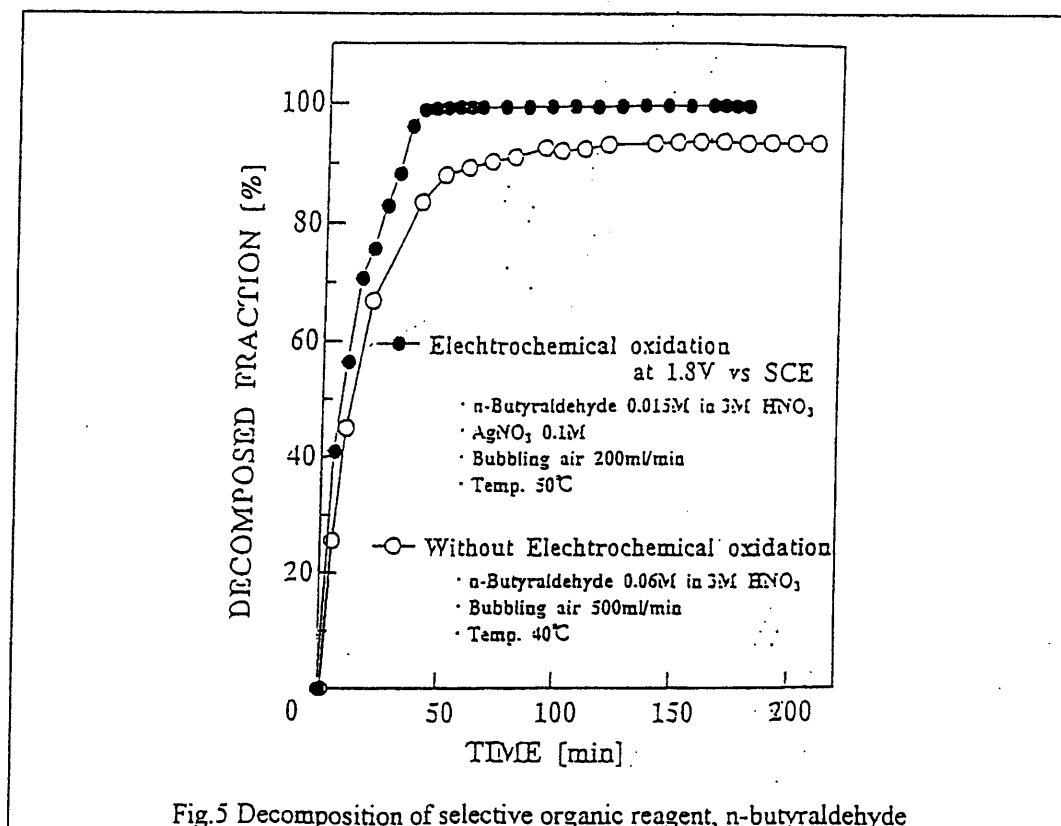
We have proposed "PARC(Partitioning Conundrum Key) process"^(2,3), as shown in Fig.3. This is a challenging program to enhance confinement capability of long-lived nuclides in a simplified reprocessing. This process is designed to separate long-lived nuclides; diffusing Np-237 and Tc-99 in extraction, volatile C-14 and I-129 in head-end, and minor actinide Am from acidic raffinate. Used acid and organic solvent are recycled in the process. Principal features are as follows,

- Simplifying the chemical process
- Enhancement of separation efficiency of the extractable Np and Tc as well as Pu and U.
- Removal of C-14 and I-129 from the off-gas in head-end .
- Recovery of the inextractable minor actinides Am as much as possible
- Recycle use the used reagent at the maximum.



4. Separation Technique of Np-237 and Tc-99

Extraction flow sheet of PARC is designed as one-cycle process based on Purex technology as the primary option, since extractant TBP exhibits sufficiently high separation ability on the major elements; uranium and plutonium. Neptunium and technetium are separated from U and Pu before U/Pu separation step in one-cycle extraction by applying innovative valence control technique⁽⁴⁾. Figure 4 shows concentration profiles obtained in a flow sheet experiment using mixer-settlers. Very high recovery rate of Np, over 99.9%, has been demonstrated by conducting selective Np reduction with a decomposable reagent butyraldehyde for a Np, Tc and U solution system. 99.98% of Np, extracted together with U in the co-decontamination step, was reduced by n-butyraldehyde and separated from U in Np separation step. More than 99.8% of Tc was separated from U in Tc separation step using 5.5M nitric acid scrub solution. In a separately conducted experiment, Pu was separated from U using iso-butyraldehyde effectively without applying hydrazine for a Np, U and Pu solution system. Decomposition of butyraldehyde has been studied in order to get rid of side effect on the separation efficiencies in the down streams. Decomposition fraction calculated from measured concentrations of total organic carbon in aqueous solution is shown in Fig. 5. It was found that more than 99% of n-butyraldehyde was decomposed within 50 minutes with silver catalyzed electrochemical oxidation. Air bubbling without electrochemical oxidation decomposed app. 90% of n-butyraldehyde in 1 hr.

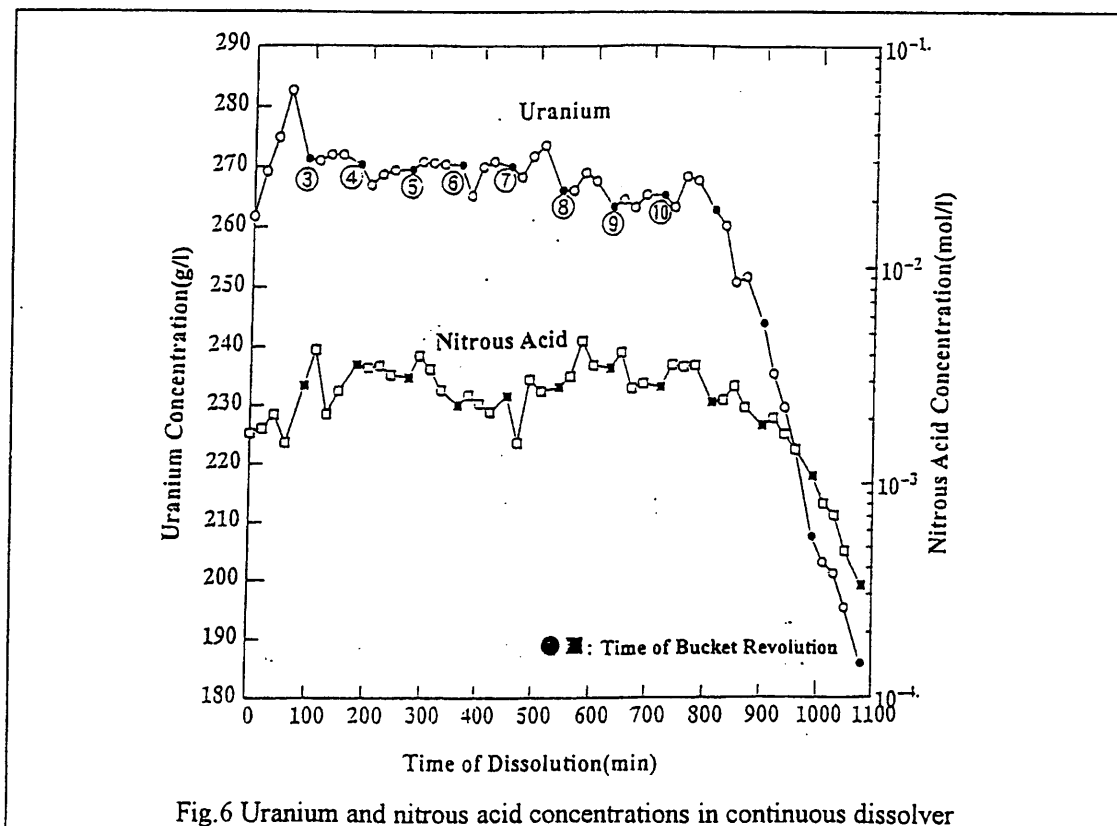


As the basis of one-cycle extraction process development, have been collected data of Np and Tc

behaviors under a standard flow sheet condition of a large scale Purex type reprocessing plant. It was found that app. 99% of Tc was extracted with U and Zr by TBP and only 1% of Tc was transferred into the raffinate of co-decontamination step. Approximately 30% of Np was transferred into the raffinate.

5. Technique for capturing I-129 and C-14

Iodine-129 is controlled to be released to dissolver off-gas(DOG) completely and removed by AgS(Silver impregnated Silica-gel). In order to assess confinement capability of volatile long-lived iodine I-129, iodine distribution in BECKY experimental equipment of head-end process(shown in Fig.2) was measured under continuous dissolution of unirradiated simulated spent fuel⁽⁵⁾. Pellets of the simulated spent fuel consist of uranium and non-radioactive fission product elements. A trace amount of radioactive iodine I-131 was added as KI to dissolver under operation. Nitrous acid concentration was high at app. 3×10^{-3} mol/l as shown in Fig.6. Most of iodine was released to DOG and captured completely by iodine adsorbent columns under condition of linear off-gas velocity up to 22 cm/s and adsorbent temperature at 150°C. Amount of iodine captured in columns is estimated to be app. 74% iodine loaded in dissolver. Less than 1% of iodine loaded was remained in fuel solution. The other iodine was distributed in HEPA filter by 11%, inside surface of pipes by 2%, insoluble residue and others by 12%, respectively. Colloidal formation with fission products such as AgI or PdI₂ is considered to be predominant retention mechanism under iodine concentration less than 10^{-6} mol/l in solution⁽⁶⁾.



Major chemical form of C-14 is carbon dioxide(CO_2)⁽⁷⁾. CO_2 is released to DOG under dissolution of spent fuel. As an adsorbent, hydrogenated mordenite, which is capable of reversible adsorption-desorption of CO_2 , has been selected after screening test of various kinds of adsorbents. Breakthrough curves of CO_2 show adsorption capacity of hydrogenated mordenite is improved under lower temperature.

6. Development of Simulation Codes

Process simulation code system ARECS(Fig.7), associated with fundamental reprocessing data-base, has been developed to simulate chemical process system composed of dissolution, off-gas treatment and extraction process. This code system is capable of simulating the behaviors of not only U and Pu but also long-lived minor nuclides such as I-129, C-14; Np-237, Tc-99 which are important in the development of nuclear fuel cycle technology. And, a computer code has been developed to simulate generation and migration of very short-lived volatile nuclide such as I-131 by spontaneous fission of TRU nuclides. TRU nuclides such as Cm-244 generate various very short-lived volatile nuclide by spontaneous fission.

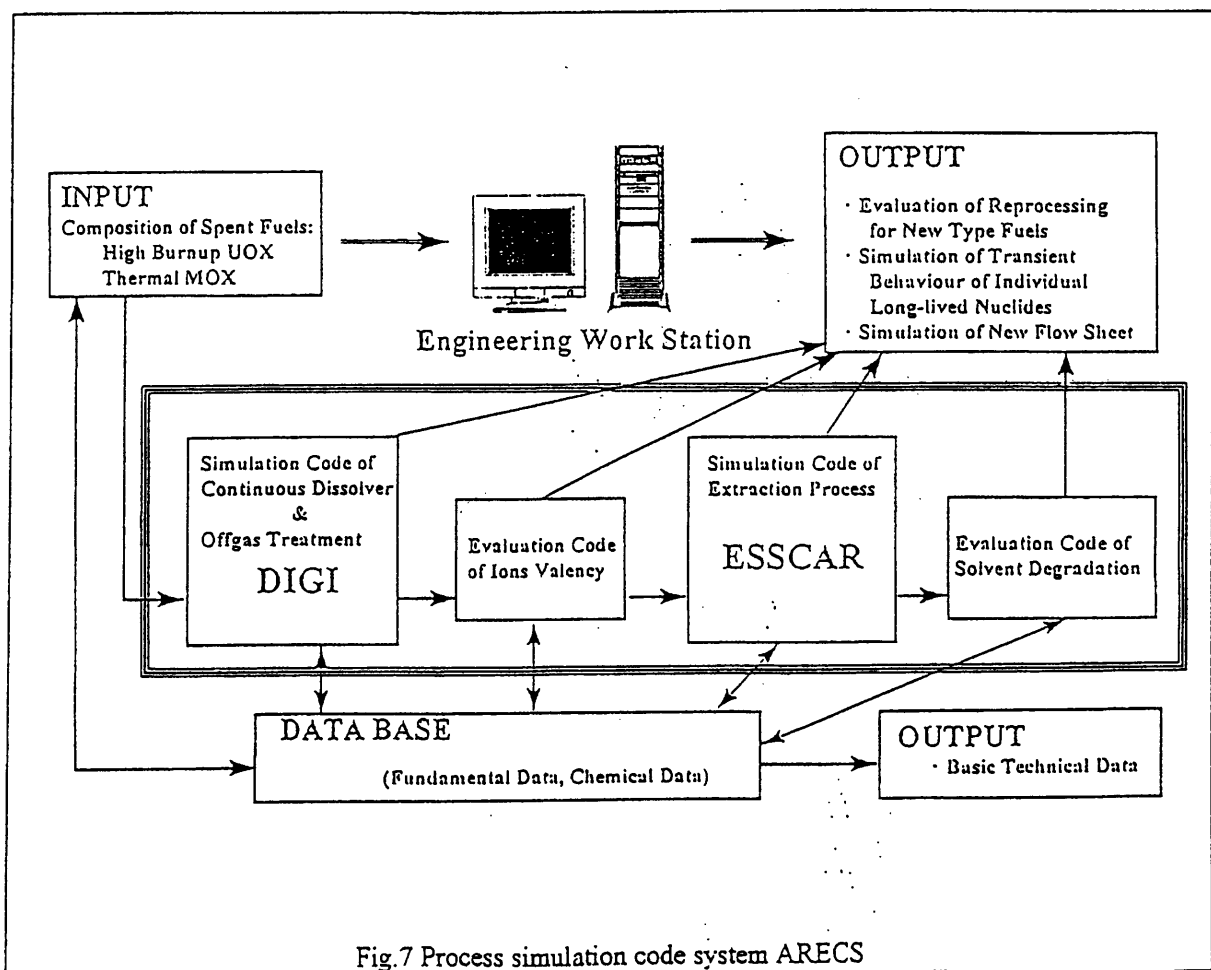


Fig.7 Process simulation code system ARECS

8. Conclusion

Development of chemical process technology for PARC concept is under way using Back-End Cycle Key Elements Research Facility(BECKY) in JAERI. High efficiency was demonstrated for separation of Np-237, Tc-99, I-129 and C-14 under a simulated condition. It is expected that technologies for enhancing confinement capability of long-lived nuclides improve the safety standard and to ease the people's anxiety about reprocessing wastes.

REFERENCES

- (1) Dreicer M. et. al., "Nuclear Fuel Cycle, Estimation of Physical Impacts and Monetary Valuation for Priority Pathway", CEPN Report No.234(1995).
- (2) M.Maeda, S.Fujine, G.Uchiyama, T.Kihara, T.Asakura, T.Sakurai, T.Tsujino, Proc.GLOBAL'95, p.556(1995).
- (3) S.Fujine, G.Uchiyama, M.Maeda, NEA/P&T report No.13 (Cadarache), p.438(1995)
- (4) G.Uchiyama, H.Asakura, M.Watanabe, S.Fujine, M.Maeda, Proc. ISEC'96, Vol.2, p.1291(1996).
- (5) T.Kihara, Y.Hashimoto, Y.Nakano, T.Sakurai, S.Fujine, JAERI-Conf 96-013, p.43(1996).
- (6) T.Sakurai, A.Takahashi, N.Ishikawa, Y.Komaki, M.Ohnuki, T.Adachi, Nucl. Technol. Vol.99, p.70(1992).
- (7) A.Leudet, P.Miquel, P.J.Goumondy, G.Charrler, Proc.17th DOE Nucl. Air Clean. Conf.

Super High Temperature Method
(Reprocessing)-Separation-Conditioning-(Disposal)

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Summary

Research and development of a simplest process of disposing of high-level radioactive waste, Super High Temperature Method, has been carried out. Batch pouring process of continually supplied fused and molten raw material of calcinated waste has been investigated. This process has successfully delivered two good products of platinum group element alloys and solidified HAW of highly reduced volume which may contain actinide elements.

1. Introduction

Two lines of research and development have been carried out as to HLLW Management. One way is to obtain solidification of HLLW to store it for several tens of years and then bring it to underground disposal. A second is that by transmutation. Namely, partitioning long-lived nuclides out of HLLW and transmuting them into nuclides of shorter lives (Research and development of retrieving useful elements out of HLLW has also been carried out and put to practical use too. Effective utilization of elements contained in HLLW is acknowledged to be an important subject. It will, however, be left out of this paper, because the principal subject here is to present the trend of HLLW management simply and clearly).

There have often been disputes between two lines of research and development. Selection of the nuclides to be put to transmutation was one of subjects of disputes. Prof. Pigford has pointed out, "Minor actinides that are thought to be highly toxic will be stably maintained under the environment of the underground disposal. In selecting the objects of transmutation, they should be fission product nuclides of relatively high mobility." There has been no true technical discussion as regards this suggestion.

Another subject of a dispute is that about the accountability. A transmutation facility will have to be operated in order to carry out transmutation of the nuclides. Operation of the facility will require energy. This energy will be supplied by nuclear power generation. Nuclear fission products will be produced by operating nuclear power plant. The total amount of toxicity of the nuclear fission products is required to be less than the amount of nuclides that is put to transmutation. Furthermore, there is another problem of the total amount of wastes generated in the whole nuclear fuel cycle mainly involved in nuclear power generation for operating the facility. Also the facilities and the installations will become wastes. The facilities to be used for transmutation of specific kinds of nuclides are bound to be contaminated. This issue either has not been put to relevant discussion. Other concerns are related to social acceptability of the under-ground disposal and realizability of transmutation. Political and generic measures to cope with these problems are being investigated in France.[1]

Apart from these discussions, technology aiming at reasonable HLLW management is subjected to research and development recently.

It is the concept of "Reprocessing-Separation-Conditioning-Disposal" together with research and development of industrial technology that makes the concept feasible. Super High Temperature Method by Japan, Partitioning-solidification technology by former USSR, proposal of Separation-Conditioning (S-C) concept

by France, SYNROC Solidification of partitioned actinides by Australia are included. Waste Minimization by U.S. also may be in the same line.[2]

The method by former USSR is in partitioning HLLW into several groups of fission products by means of extraction or ion exchange and solidifying each group separately. In one of these processes HLLW is partitioned into fission products and transition metal elements (Zr, Mo, Pd etc.). FPs are vitrified. Transition metals are cemented. Other than vitrification, Synroc Solidification by melting has also been developed. Cold crucible method has been developed as for solidification technique. In 1996, the First Committee of Nuclear Ministry of Russia (MINATOM) decided to extend this method further.

France established a law in order to proceed research and development concerning High Level Waste Management with centralized concern about waste management including P/T. An annual report of each organization which checks and reviews the research and development activities is published in accordance with this law. The first report in 1995 describes the concept of Separation-Conditioning (S-C). France considers the reprocessing process a unified process of reprocessing and waste management. (They are not necessarily treated in the same way in other countries. Reprocessing plants are closed in those countries and management of HLLW in hand is a subject of concern). France is making an effort to reduce the output of radioactive wastes to an utmost limit in reprocessing process based on the above mentioned concept.

Development of a cold crucible is being carried out in order to cope with obsolescence of the melting furnace. This technique is in the stage of technical completion.

In Australia, Research of Synroc solidification of actinides separated from HLLW is being carried out. Development of the above mentioned solidification technique by Russia and development of the oxide solidification technique by Super High Temperature Processing Method by Japan that will be described later are both in the line leading toward the method of solidification unexpectedly similar to Synroc Concept created by Prof. Ringwood.

In the United States research and development is being carried out based on the idea of minimizing the waste generated in the reprocessing plant for military purposes. However, this idea is not carried through HLLW management. A huge vitrification plant is being brought into operation. At INEL, on the other hand, research and development of Separation-Conditioning is just being carried out. Structuring of the overall concept of Waste Minimization of HLLW may be required.

As to S-C in Japan, partitioning by wet method and solidification of each group was proposed by JAERI. Development of partitioning technique is being mainly carried out at JAERI, while development of vitrification technique is not being carried out.

Super High Temperature Method in Japan is a new S-C technique by metallurgical procedure. In the beginning, this method was started aiming at solidification of HLLW without addition of matrix material like glass. It was discovered in the stage of research that highly exothermic FP, cesium, is vaporized and separated, that elements of the platinum group are reduced by adding reducing agents and separated as alloys, and that other FP oxides (including actinides) are melted and solidified.

Selection of the reductant is an important subject in Super High Temperature Method. Platinum group elements are those which can be easily reduced among HLLW FPs. Insoluble materials in spent fuels are small particles of alloys formed by the platinum group elements in FP under the condition of oxygen shortage.

Platinum group elements are reduced when the calcine is heated in the inactive atmosphere, and small

particles of alloys are formed. Small particles of alloys are dispersed in the calcine of oxides of FP elements which are not reduced under this condition. When the calcine is heated with addition of reductant, the whole system is melted and the metal and the oxide phases are separated into upper and lower layers. The principal action of the reductant consists of reduction of the transition metal elements included in FP. As the results of reaction, the transition metal elements including platinum group elements form alloys of relatively low melting points. And also, the reductant produced by reaction is an oxide itself. This oxide forms a composite oxide of relatively low melting point.

The reductants are selected from elements with intermediate value of the standard free energy of oxide phase formation and that of metal phase formation. Also, it is chosen to be one of elements which bring about the phenomenon of lowering of melting point. Results of selection of favorable candidate elements are boron, aluminum, silicon, and titanium.

When boron is adopted the oxide phase is of poor water resistance. When aluminum is adopted lowering phenomenon of melting point is relatively weak, thus the temperature of treatment is required to be brought up.

When silicon is used, the oxide phase becomes glassy. Namely, vitrification is attained within Super High Temperature Method. When titanium is used, separation of two phases is effective, and the oxide phase is water resistant also. Therefore, at this time, silicon and titanium are favorable as reductant.

Processing with titanium compounds were adopted for current experiments. Titanium alloys, titanium carbide, and titanium nitride are applicable as reductant of titanium compounds. Since titanium alloy is in the form of particle, it is feared that homogeneity of mixing with calcine might be insufficient. Since titanium carbide and titanium nitride are in stable powder form, mixing with calcine will be easy. Titanium nitride has been chosen this time.

Reductants are titanium or reducing titanium compounds. Titanium is turned into titanium oxide as the result of reaction and introduced into the oxide phase. Titanium constitutes composite oxides with rare earths, alkaline earths, zirconium, etc. that constitutes oxide phase. By this method, separation of cesium, retrieval of elements of the platinum group, and high volume reduction and solidification are achieved through simple procedures.

In this report, results of experiments concerning continuous supply of simulated calcine-retrieval of the platinum group elements by batch flow down process-preparation of solidification of highly reduced volume will be presented.

2. Process of Super High Temperature Method

The Process of Super High Temperature Method is as follows:

HLLW → Calcination → Sublimation → Reduction → Melting → Pouring → Separation → Storage

High level liquid waste is brought into composite oxides of fission products through calcining process. Cs etc. are separated through vaporization of the calcine.

Oxides of platinum group elements are reduced into metallic phase and partitioned from the oxide phase of rare earth elements and other elements by processing at 1000 C with the reductant of titanium nitride. The system is then processed by melting at 1600 C in order to be partitioned into two phases of metal and oxide.

3. Objectives of the experiments

Up to this stage, experiments have been carried out using 20 g of simulated calcine and a crucible of 30 ml in order to determine the conditions of reduction and fusion-separation of the platinum group elements. Next stage will be developing the technological facilities. A cold crucible technology is presumed for the melting

facility. As a preliminary experiment for this process, a method of heating the crucible for melting by high frequency induction and subsequently melting the calcine by conduction heating from it has been investigated. In the process of melting, the calcine is continually supplied. As to crucibles, there are two ways of methods one of which is using the same crucible for melting and also for solidifying, and another is to provide these two sorts of crucibles separately. By the former method the surface portion of the solidification will not be melted homogeneously. It is required to establish a method of obtaining a satisfactory solidification by the latter. Two procedures were examined in comparison.

4. Experiments

Sample material:

Calcine of equivalent composition to that after sublimation was prepared by blending commercially available oxides of reagent grade. The amount of the reagent is several hundreds of grams.

Heating:

The melting temperature is 1600C. The apparatus is shown in Fig. 1.

Three ways of heating were carried out.

1. A carbon crucible was heated by high frequency induction method.
2. A boron nitride crucible placed in a carbon crucible which was heated by high frequency induction was in turn heated by conduction method.
3. A method to pour the melt from the nitride crucible as above into the receptacle installed underneath (Fig.2).

Melting:

The sample material was melted by continuously feeding it into the crucible in terms of a vibration feeder.

Pouring:

In the three methods as mentioned above, molten sample material was poured into the receiving crucibles (kept at protection temperature) through a bottom hole of the melting crucible.

Solidification:

Sample material was released to be solidified by deenergizing the protective heating of the melting crucible or the receiving crucible.

5. Results and discussion

- (1). The method of high frequency induction heating the carbon crucible.

In this case the metal and the oxide phases are separated into the upper and the lower layers. However, the state of separation is not clear-cut. Also there are voids in the oxide phase. This is thought to be attributed to the reduction reaction caused by the crucible material, carbon.

- (2). The method of conduction heating the nitride crucible which is placed in a carbon crucible heated by high frequency induction.

In this case the metal phase and the oxide phase are separated into upper and lower phases. Separation of the metal ingot is appreciable also. No void is observed in the oxide phase. It is thought because the crucible material, boron nitride does not generate reduction reaction that gives out bubbling action. However, the surface of the oxide phase is not clean.

- (3). The method of pouring down into the receiving crucible installed underneath from the boron nitride crucible in the procedure (2).

In this procedure, the metal phase and the oxide phase are separated cleanly. The metal ingot is also separated well. There is no void observed in the oxide phase. The surface of the oxide phase is clean (Fig.3).

It has been confirmed that normal metal and oxide layers can be constituted by the process of continuous feed and batch pouring. Feasibility of formation of normal products has been demonstrated by making it possible to melt the calcine at high temperature in terms of the cold crucible process, although the melting in this experiment was carried out by thermal conduction method.

References:

- [1] The first report, National Evaluation Commission, France, 1995
- [2] Misato Horie, High Level Radioactive Waste Treatment: State of Current Research and Development, (PNC TN9420 94-0190, 1995)

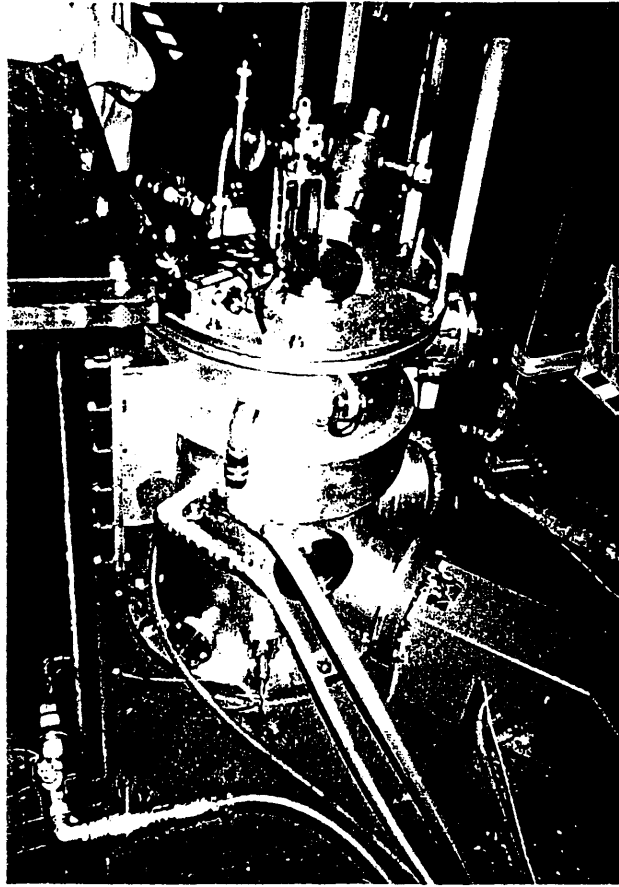


Fig.1 The experimental apparatus

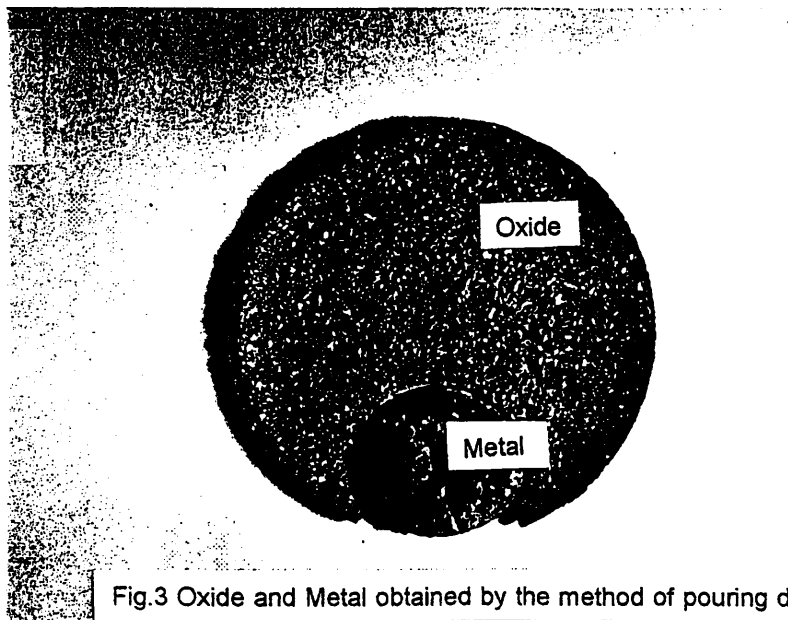


Fig.3 Oxide and Metal obtained by the method of pouring down

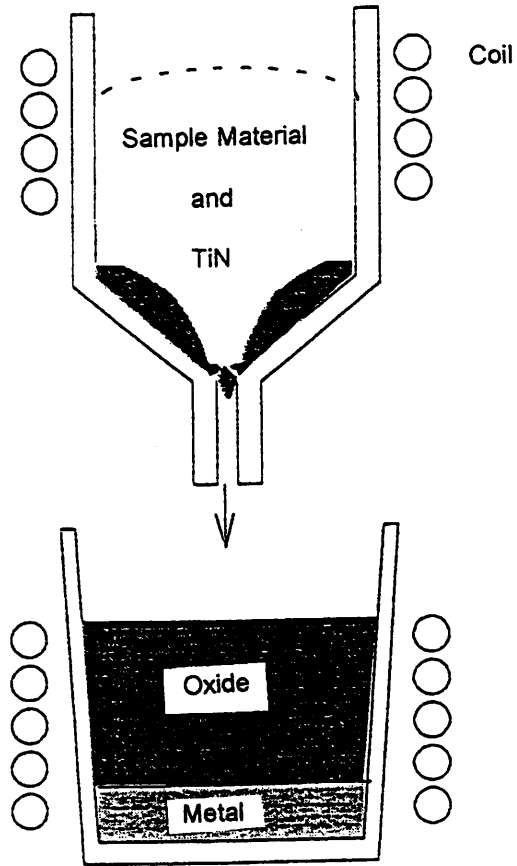


Fig.2 Crucibles of the method of pouring down

BASIC STUDY OF PHOTOCHEMISTRY FOR APPLICATION TO NUCLEAR FUEL CYCLE TECHNOLOGY

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Abstract

In this study, we have accomplished for the first time the photochemical valence adjustment of Pu and Np for the separation and coextraction of these elements in a nitric acid solution using UV light irradiation. Also, the separation and coextraction of Pu and Np were substantiated in principle by the photochemical and solvent extraction operations. The separation and coextraction of Pu and Np by solvent extraction using 30% TBP/n-dodecane were carried out during and after the photochemical valence adjustment. By only one photochemical separation operation, about 86% of Pu and about 99% of Np were distributed into the organic phase and the aqueous phase, respectively, and then by only one photochemical coextraction operation, about 86% of Pu was distributed together with about 99% of Np into the same organic phase. Based on these experimental data, we determined that the photochemical oxidation reaction was due to the photoexcited nitric acid species, $^*NO_3^-$. Using the strong oxidative ability of this species, the photochemical dissolution of UO_2 powder in a nitric acid solution by UV light irradiation was also accomplished for the first time at room temperature (20 °C). Photochemical dissolution tests of UO_2 powder ranging 1 mg to 100mg suspended in 2 ml of 1-6M HNO_3 solutions were carried out at room temperature using a Hg lamp. From the results of the tests, 10mg of UO_2 powder was completely dissolved in 2ml of a 3M HNO_3 solution at 20°C under an irradiation rate of $1.3W/cm^2$ for 40min.

1. Introduction

Most nuclear fuel reprocessing plants have been adopting the PUREX process technologies. Uranium(U) and plutonium(Pu) in spent nuclear fuel are recovered and refined using these technologies with a high recovery efficiency.

Neptunium(Np), however, is distributed on both sides of the nuclear fuel production and also in highly radioactive aqueous waste. This phenomenon is caused because of the difficulty in valence adjustment of Np using various chemical reagents in nitric acid solution⁽¹⁾⁻⁽³⁾.

It is generally supposed that photochemical techniques offer a potential for selectivity in systems where chemical methods offer little selectivity. From that point of view, photochemical studies of U, Pu and neptunium(Np) have been carried out for separation and reprocessing techniques mainly in the USA. These studies can be divided into several categories which are the studies for the photochemical behavior of nuclear fuel⁽⁴⁾⁻⁽⁸⁾, Np⁽⁹⁾⁻⁽¹²⁾ and photochemical reprocessing technologies⁽¹³⁾⁻⁽¹⁵⁾. These studies, however, only describe the fundamental photochemical behavior of these elements' valences and did not carry out quantitative valence adjustment for the separation and coextraction of Np with experimental data. They did not then discuss the mechanism of the photochemical redox reaction such as our suggestion involving a photoexcited nitric acid species⁽¹⁶⁾. We report the results of the quantitative photochemical separation and coextraction experiments of Pu and Np and then we have considered that the photoexcited nitric acid species, $^*NO_3^-$, contributed most effectively to the oxidation reactions of Pu and Np. These reactions are caused by a higher redox electrode potential of the photoexcited species than that of the ground state species, NO_3^- ⁽¹⁷⁾⁻⁽¹⁹⁾. Based on the results, we have also attempted to use the strong oxidative ability of $^*NO_3^-$ for the dissolution reaction of UO_2 powder at room temperature⁽²⁰⁾.

2. Experimental

2.1 Apparatus and analysis

As the light source, a super high-pressure Hg lamp (WACOM Co., Ltd. BMO-250DI) was used in the wavelength range of 250 nm to 600 nm. The maximum output intensity was 1.5 W/cm^2 . The homogeneity and temperature of the test solution were kept constant using an electric temperature stabilizer and a magnetic stirrer during the tests.

The valences of Pu and Np in nitric acid solutions were analyzed using a spectrophotometer (Shimadzu UV-1200).

2.2 Preparation of test solution and UO_2

The Pu stock solution was previously refined using an anion exchange column americium(Am) was removed from the solution. The concentration of Pu in the solution was calculated using its specific α -radioactivity obtained by mass spectrometric analysis and the data obtained by the α -ray counting method. The analyzed isotopic composition is shown in Table 1.

The α -radioactive purity of Np-237 in the Np stock solution was 100.0% and the concentration of Np in the solution was also determined by the α -counting method.

The test solutions of Pu and Np mixed solution containing additional reagents such as hydroxylamine nitrate(HAN) and hydrazine(HDZ) or urea, which were all reagent grade, were prepared by mixing their stock solution and additional reagents for about 10 mins. before the start of the irradiation test.

The specific properties of the UO_2 powder used for the tests are shown in Table 2.

Table 1 Isotopic composition of Pu used in test

Nuclide	Pu-238	Pu-239	Pu-240	Pu-241	Pu-242
Abundance (Wt%)*	0.148	75.79	21.51	1.855	0.697

* : Analyzed on Feb. 10, 1993

Table 2 Specific properties of UO₂ Powder used in tests

U content (%)	O / U	Ave. par. size(μ m)	Density (g/cm ³)	Spec. surf. area(m ² /g)
87.73	2.06	0.68	1.96	4.28*

* : BET method

2.3 Experimental procedure

The photochemical valence adjustment and solvent extraction test experiments were carried out as follows.

(1) Photochemical valence adjustment

For Pu and Np in a nitric acid solution, the extractable valences are Pu(IV and VI) and Np(IV and VI), while the inextractable valences are Pu(III) and Np(V) with 30 % TBP/n-dodecane⁽²¹⁾. It is the purpose of this study to determine whether the photochemical technique can adjust the valences of Pu and Np to suitable valences for their separation or coextraction.

For the separation experiments, the initial valences in the test solutions of Pu and Np were previously adjusted to Pu(III) and Np(V) using HAN and HDZ before the light irradiation. It was then evaluated whether Pu(III) could be photooxidized to Pu(IV) and Pu(VI)(extractable valences) by the irradiation, and Np(V)(inextractable valence) remained at the same valence during the light irradiation. On the other hand, during the coextraction experiments, the initial valences in the test solutions containing urea were Pu(IV, VI) and Np(V). It was then evaluated whether the light irradiation could completely adjust them to Pu(IV, VI) and Np(VI)(all of these valences being extractable). Furthermore, their valence behavior was also examined under no light irradiation(dark reaction) for the comparison to that under the light irradiation.

Two ml of the test solution was placed in a 1cm square quartz cell generally used for photospectrometry. The cell was then irradiated using the Hg lamp for an appropriate time. The changes in the Pu and Np valences were measured by the photospectrometer at specified intervals using the quartz cell containing the test solution. In these tests, the experimental variables included the irradiation rate (0, 0.05, 0.15 and 1.45 W/cm²) and the concentration of HNO₃ (0.4, 1, 2 and 3 M).

(2) Solvent extraction

First, for the separation of Np from the Pu and Np mixed solution, 1 ml of the 2M HNO₃ solution containing Pu (1.0×10^{-3} M), Np (1.0×10^{-3} M) and HAN+HDZ (8.0×10^{-2} M each), and 1 ml of 30 % TBP/n-dodecane were placed in the quartz cell. The cell was set into the cell holder which contained the temperature stabilizer and stirrer, and the light irradiation and the solvent extraction were then started simultaneously.

In the case of the coextraction operation, 1 ml of the 3 M HNO₃ solution containing Pu (1.0×10^{-3} M), Np (1×10^{-3} M) and urea (8.0×10^{-2} M), and 1 ml of 30 % TBP/n-dodecane were used. In one case, the light irradiation and the solvent extraction were simultaneously carried out. In the other case, the solvent extraction operation was done after the photochemical valence adjustment.

After specified intervals of the solvent extraction operation, aliquots of both phases were taken out of the other cell and analyzed using the spectrophotometer.

(3) Photochemical dissolution

1-100mg of UO₂ powder are weighed precisely and are placed in a quartz cell, normally used in photospectrometry, containing 2ml of a nitric acid solution. The solution is then irradiated using the Hg lamp, and the absorption spectrum of the solution is measured at the appropriate irradiation time.

The photochemical dissolution fraction of the UO₂ powder is calculated by the ratio between the absorbances A_i and A_t of UO₂²⁺ at 425nm and an arbitrary time i and t , which is the complete dissolution time at t , as follows.

$$\text{Dissolution fraction(\%)} = \frac{A_i}{A_t} \times 100 \quad \text{-----(1)}$$

A_i : Absorbance at time i .

A_t : Absorbance at time t of the complete dissolution time.

The concentration of nitrous acid, HNO_2 , a by-product of the UO_2 dissolution reaction, is also determined by the absorbance of the test solution at 370nm and a calibration curve which is obtained by analysis of standard concentrations of HNO_2 from 1.0×10^{-3} to 5.0×10^{-2} M.

The temperature and the homogeneity of the solution are kept constant with a temperature stabilizer and a magnetic stirrer during an irradiation test.

The experimental variables are the irradiation rate whose levels are 0, 0.7 and 1.3 W/cm^2 , the concentration of HNO_3 whose levels are 1, 3 and 6M and the weight of the UO_2 powder whose levels are 1, 10 and 100mg.

3. Results and discussion

3.1 Photochemical valence adjustment

For the photoreaction tests, three kinds of experimental conditions for the Pu and Np mixed solution were adopted

- ① the examination of the photochemical behavior of Pu and Np valences in the nitric acid solution without the addition reagent,
- ② the valence adjustment for the separation of Np from Pu, and
- ③ the valence adjustment for the coextraction of Np with Pu.

(1) Photochemical reaction of Pu and Np without addition reagent

Figure 1 shows the results of the photochemical reaction of Pu and Np in 3 M HNO_3 solution containing no addition reagent under the conditions of 1.40 W/cm^2 irradiation rate and 20°C .

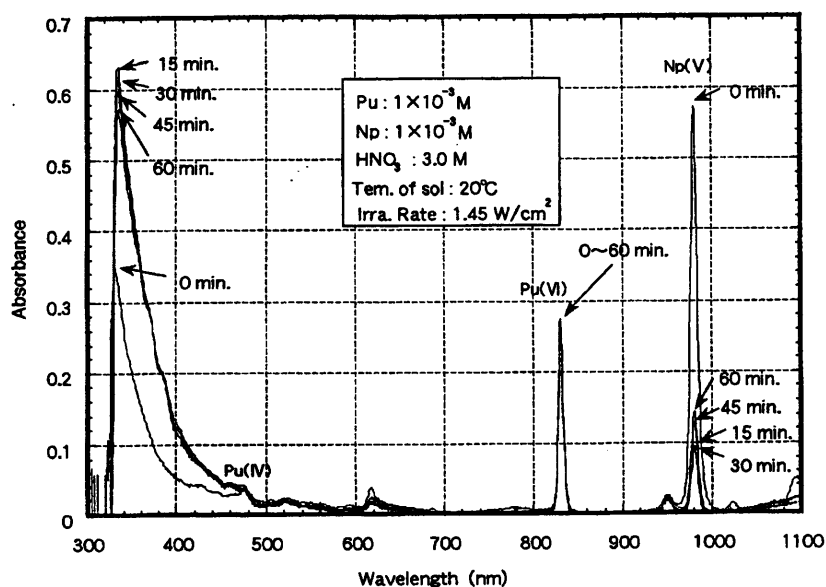
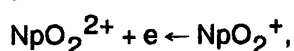
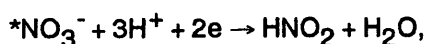


Fig.1 Change in absorption spectra by photochemical reaction in Pu, Np mixed 3M HNO_3 solution containing no additional reagent vs. irradiation time

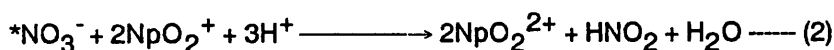
As seen in this figure, around 85 % of Np(V) decreased and was photooxidized to Np(VI) within 15 mins. After that, the reverse reaction of Np(VI)→Np(V) progressed predominantly, and then Np(V) gradually increased. This phenomenon is caused by the relationship between the oxidation reaction of the photoexcited nitric acid species⁽¹⁶⁾, *NO₃⁻, and the redox reaction by nitrous acid⁽²²⁾, (23) of the photolysis product as follows.

- The oxidation reaction of Np(V)→Np(VI) by *NO₃⁻



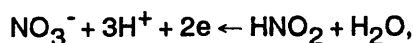
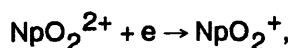
↓

*k_{5→6}



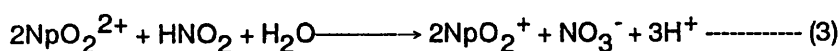
where *k_{5→6} : photochemical reaction rate constant.

- The reduction reaction of Np(VI)→Np(V) by HNO₂



↓

k_{6→5}



where k_{6→5} : reaction rate constant.

Pu(IV) is also photooxidized to Pu(VI) by the photoexcited nitric acid species and a part of the Pu(VI) is reduced to Pu(IV) by nitrous acid⁽²²⁾.

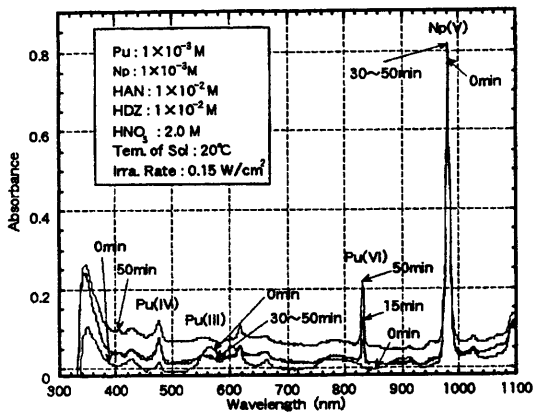
As seen in Figure 1, if the decomposition reagents such as HDZ⁽²⁴⁾ or urea⁽²⁵⁾ were not contained in the Pu and Np mixed solution, the complete valence adjustment for their separation or coextraction would not be attained using the Hg lamp irradiation.

(2) Photochemical valence adjustment for separation

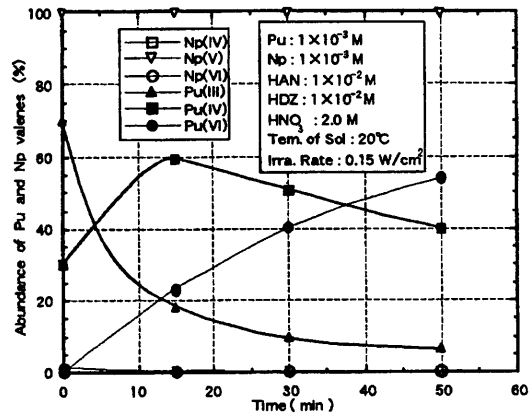
1. Effect of concentration of HNO₃

Mixed solutions of 1x10⁻³ M Pu and Np containing reductants, 1x10⁻² M of HAN and HDZ, were prepared by changing the HNO₃ concentration to 0.4 M, 1 M, 2 M and 3 M. These solutions were then examined at the irradiation rate of 0.15 W/cm². Figures 2 and 3 show the results of the irradiation tests at concentrations of 2 M and 3 M HNO₃, respectively. All of the results under the condition of each acidity are shown in Table 3. These data are calculated as the average reaction rate as follows.

$$\text{Average photochemical reaction rate (M/min)} = \frac{\text{Variation value (mol)}}{\text{Reaction time (min)}} \text{ ----- (4)}$$

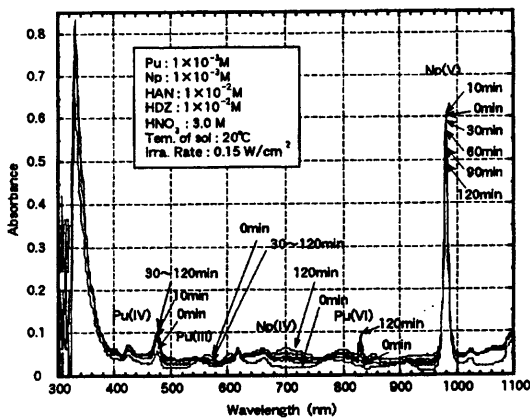


(a) Change in absorption spectra

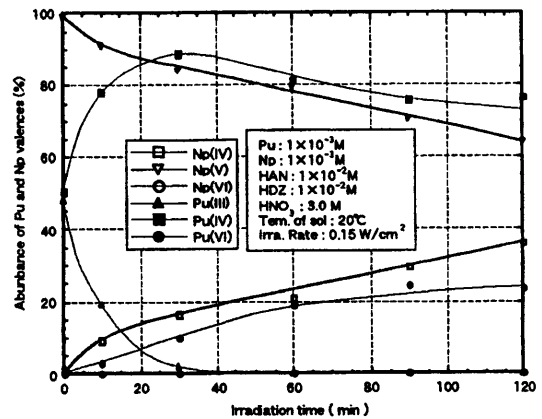


(b) Change in abundance of valences

Fig.2 Change in Pu and Np valences by photochemical reaction in 2M HNO₃ containing HAN and HDZ vs. irradiation time



(a) Change in absorption spectra



(b) Change in abundance of valences

Fig.3 Change in Pu and Np valences by photochemical reaction in 3M HNO₃ solution containing HAN and HDZ vs. irradiation time

Table 3 Change in photochemical reaction rate according to increase in acidity

Acidity(HNO ₃) (M)	Average photochemical reaction rate (mol / min)*			
	Pu(III)→Pu(IV)	Pu(IV)→Pu(VI)	Np(V)→Np(IV)	Np(V)→Np(VI)
0.4	1.07 × 10 ⁻⁶	6.76 × 10 ⁻⁷	-	-
1	5.78 × 10 ⁻⁶	6.10 × 10 ⁻⁶	-	-
2	1.27 × 10 ⁻⁵	1.07 × 10 ⁻⁶	-	-
3	1.29 × 10 ⁻⁵	1.87 × 10 ⁻⁶	2.06 × 10 ⁻⁶	-

* : Average photochemical reaction rate was calculated as ratio of change value in concentration of Pu or Np per reaction time.

[Pu] and [Np] = 1 × 10⁻³ mol/dm³, [HAN] and [HDZ] = 1 × 10⁻² M, Irra. rate = 0.15 W/cm².

- : Can not be observed.

As shown in this table, the higher the acidity, the faster the photochemical reaction rate except only for the data of Pu(IV)→Pu(VI) at 3 M HNO₃.

In the case of Np, all of the results at lower than 2 M HNO₃ did not change at all in both cases of the oxidation and reduction reaction of Np(V). This is because an exception occurred due to the strong reducing ability of HAN and HDZ only at the highest acidity of 3 M HNO₃ even though the test solution was irradiated at the rate of 0.15 W/cm². On the other hand, Np(V) was continuously reduced to Np(IV) even after Pu(III) had completely disappeared after 40 mins. irradiation as shown Fig. 3-(b). This phenomenon indicates that Np(V) was not reduced by Pu(III) only, which is different from the results reported by Koltunov et al. (26). After about 40 mins. irradiation, the reductants are only HAN and HDZ. Therefore, it can be considered that these reductants reduced Np(V) to Np(IV). However, we do not understand why Np(V) was not reduced to Np(IV) under the same condition of only Np(V) 3 M nitric acid solution as previously mentioned. This reason has to be clarified by future experiments.

2. Effect of light irradiation rate

The results of the irradiation tests using the Pu and Np mixed 3 M HNO₃ solution containing 1 × 10⁻² M of HAN and HDZ and changing the irradiation rates to 0.05, 0.15, and 1.45 W/cm² are shown in Table 4. These results are shown as the values of the average photochemical reaction rate. As seen in this table, the increase in the irradiation rate hastened the reaction rate of the photochemical oxidation of Pu and Np.

The reducing reaction of Np(V)→Np(IV) and the oxidation reaction of Np(V)→Np(VI) are shown in Eqs.(5), (6) and (7), respectively.

Table 4. Change in photochemical reaction rate according to increase in irradiation rate

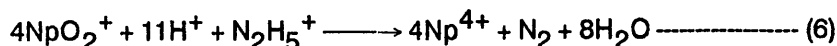
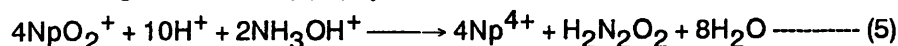
Irradiation rate (W/cm ²)	Average photochemical reaction rate (mol / min)*			
	Pu(III)→Pu(VI)	Pu(IV)→Pu(VI)	Np(V)→Np(IV)	Np(V)→Np(VI)
0.05	7.33 × 10 ⁻⁶	9.99 × 10 ⁻⁷	9.13 × 10 ⁻⁷	-
0.15	1.29 × 10 ⁻⁵	1.87 × 10 ⁻⁶	2.06 × 10 ⁻⁶	-
1.45	5.52 × 10 ⁻⁵	7.55 × 10 ⁻⁶	-	3.80 × 10 ⁻⁶

* : Average photochemical reaction rate was calculated as ratio of change value in concentration of Pu or Np per reaction time.

[Pu] and [Np] = 1 × 10⁻³ mol/dm³, [HAN] and [HDZ] = 1 × 10⁻² M, Irra. rate = 0.15 W/cm².

- : Can not be observed.

• Reducing reaction of Np(V) by reductants



• Oxidation reaction of Np(V) by the photoexcited nitric acid species, *NO₃⁻.



From the comparison among each variable level in Table 4, it was found that the photooxidation rates of Pu(III)→Pu(IV) and Pu(IV)→Pu(VI) became faster, and then the reducing reaction of Np(V) → Np(IV) based on Eqs. (5) and (6) became inferior compared to the photooxidation reaction of Np(V)→Np(VI) based on Eq. (7) according to the increase in the irradiation rate.

As shown in these results, the most suitable irradiation rate condition was 0.15 W/cm² for the separation of Np from Pu in the 2 M HNO₃ solution, which contains 1×10⁻³ M Pu and Np and also contains 1×10⁻² M HAN and HDZ.

(3) Photochemical valence adjustment for coextraction

The experiments on the photochemical valence adjustment for the coextraction of Pu and Np were carried out using the Pu, Np mixed solution containing the additional reagent of 8×10⁻² M urea and 1×10⁻³ M of Pu and Np in 3 M HNO₃. The irradiation rate was 1.45 W/cm². The results are shown in Figs. 4-(a) and (b). As seen in Fig. 4-(a), the absorption spectrum of Np(V) at 980 nm disappeared up to 10 mins. irradiation, and only the minor absorption spectrum of Pu(VI) at 980 nm remained. Np(V) was completely photochemically oxidized to Np(VI). Pu(IV) was also photochemically oxidized to Pu(VI) and decreased according to the irradiation time. These results indicate that all valences of Pu and Np were photochemically adjusted to the coextractable valences for 30 % TBP/n-dodecane under the experimental conditions shown in this study.

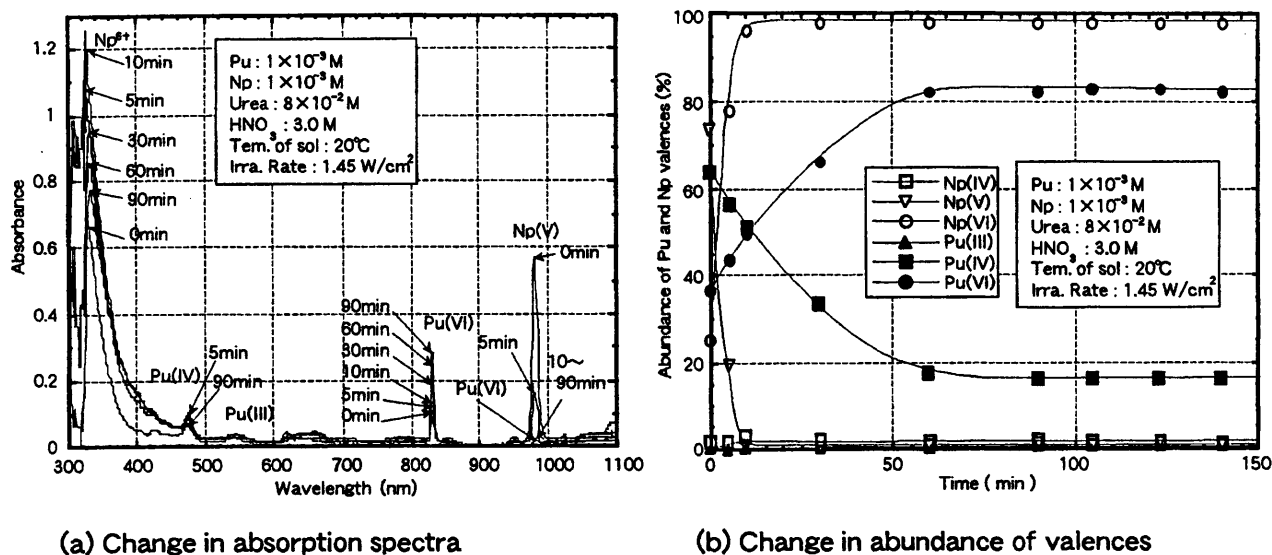


Fig.4 Change in absorption spectra by photochemical reaction in Pu, Np mixed 3M HNO₃ solution containing urea vs. irradiation time

(4) Dark reaction after valence adjustment

In general, there is at least an interval of several hours between the valence adjustment and the solvent extraction operation during an actual process. If the adjusted valences change during this interval, the efficiency of the separation or coextraction becomes low. Therefore, it is important to determine the stabilities of the adjusted valences in a nitric acid solution.

Figure 5 shows the results of the dark reaction, the stabilities of the adjusted valences after stopping the light irradiation of the Pu and Np mixed solution containing HAN and HDZ in 3 M HNO₃. As seen in this figure, Pu(VI) was rapidly reduced to Pu(IV), and then part of the Pu(IV) was further reduced to Pu(III) after stopping the light irradiation. Np(V) was also rapidly reduced to Np(IV). As shown by these results, the adjusted valences of Pu and Np in the 3 M HNO₃ solution containing HAN and HDZ were not stable. Therefore, in the case of the separation, the solvent extraction has to be immediately carried out after the operation of the photochemical valence adjustment or be simultaneously carried out during the light irradiation.

Figure 6 shows the results of the dark reaction after stopping the light irradiation of the Pu and Np mixed solution containing urea in the 3 M HNO₃. As seen in this figure, all of the photochemically adjusted valences were entirely stable after stopping the light irradiation for more than 4 hours. Based on these results, there is no problem for the solvent extraction operation even several hours after the valence adjustment in the case of coextraction.

3.2 Solvent extraction for separation and coextraction of Np from/with Pu

During or after the light irradiation, the solvent extraction operation was examined using 30 % TBP/n-dodecane to confirm whether Pu and Np can be separated or coextracted.

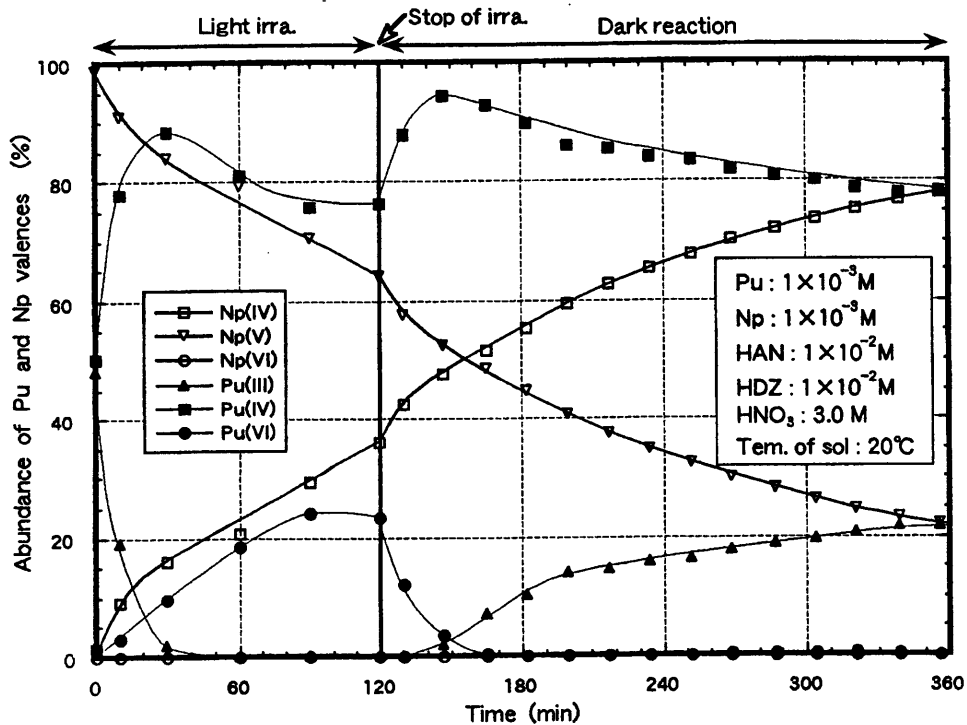


Fig.5 Stability of valences of Pu and Np in 3M HNO₃ solution containing HAN and HDZ after stopping light irradiation

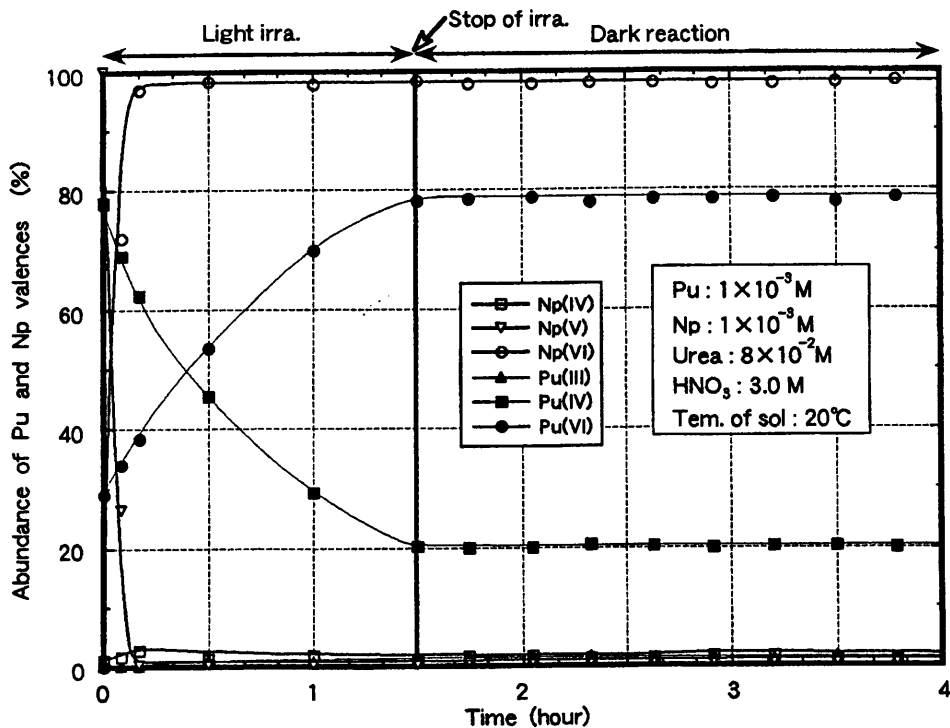


Fig.6 Stability of valences of Pu and Np in 3M HNO₃ solution containing urea after stopping light irradiation

(1) Separation

The results of the separation by the simultaneous operations of irradiation and solvent extraction are shown in Table 5. As seen in this Table, Pu(III) in the aqueous phase completely disappeared after 15 mins. operation. Pu(III) was photochemically oxidized to Pu(IV) and Pu(VI) like the results when only the operation of the valence adjustment was carried out, and Pu having these valences was then simultaneously extracted into the organic phase. In the case of Np, most of the initial Np(V) in the aqueous phase did not change and remained in the aqueous phase depending upon its specific distribution coefficient in the solvent. About 98 % of the initial Pu(III) was photooxidized to Pu(IV) or Pu(VI) and 86.2 % of Pu was extracted into the organic phase during 30 mins. During the irradiation and extraction, Pu(IV) in the organic phase gradually decreased, and Pu(VI) inversely increased. This oxidation reaction of Pu(IV) to Pu(VI) in the organic phase may be due to the photoexcited nitric acid species in the aqueous phase being in contact with both phases. The clear reason for this phenomenon must be defined by detailed data obtained in the future.

Consequently, 87.1% of Pu was extracted into the organic phase and 99.8% of Np remained in the aqueous phase only using one operation of the simultaneous irradiation and extraction.

Table 5 Results of simultaneous operation of irradiation and solvent extraction for separation of Np from Pu

(a) Abundances of Pu valences in both phases vs. operation time

Valence		Abundance (%)			
		Just before operation	Time of simultaneous ope. of irra. and ext.		
			15min	30min	50min
Aq.	Pu(III)	70.4	3.4	1.5	0.4
	Pu(IV)	29.6	8.1	4.7	3.0
	Pu(VI)	<0.1	4.7	7.7	9.6
Org.	Pu(III)		<0.1	<0.1	<0.1
	Pu(IV)	–	71.5	45.8	26.9
	Pu(VI)		12.2	40.4	60.2
	Gross Pu in Org.	<0.1	83.7	86.2	87.1
	in Aq.	100.0	16.3	13.9	13.0
	Org. / Aq.	–	5.13	6.10	6.70

Pu : 1.0×10^{-3} M
 Np : 1.0×10^{-3} M
 HAN : 1.0×10^{-2} M
 HDZ : 1.0×10^{-2} M
 HNO₃ : 2.0M
 Temp. : 20°C
 Irra. rate : 0.15 W/cm²

(b) Abundances of Np valences in both phases vs. operation time

Valence		Abundance (%)			
		Just before operation	Time of simultaneous ope. of irra. and ext.		
			15min	30min	50min
Aq.	Np(IV)	<0.1	<0.1	<0.1	<0.1
	Np(V)	100.0	99.1	98.5	99.8
	Np(VI)	<0.1	<0.1	<0.1	<0.1
Org.	Np(IV)		<0.1	<0.1	<0.1
	Np(V)	–	0.9	1.52	0.2
	Np(VI)		<0.1	<0.1	<0.1
	Gross Np in Org.	<0.1	0.9	1.52	0.2
	in Aq.	100.0	99.1	98.5	99.8
	Org. / Aq.	–	0.009	0.015	0.002

(2) Coextraction

1. Solvent extraction operation after photochemical valence adjustment

As shown in chapter 3.3, Np(VI), Pu(IV) and Pu(VI), which were photochemically adjusted in 3 M HNO₃ solution containing urea, were very stable for more than 4 hours even though the light irradiation stopped. The solvent extraction test was then carried out after the valence adjustment with the irradiation rate at 1.45 W/cm², using the 1×10⁻³ M of Pu and Np mixed solution containing 8×10⁻² M of urea in 3 M HNO₃ and 30 % TBP/n-dodecane. The results are shown in Table 6. This table shows the changes in the abundance(%) of each valence in both the aqueous and organic phases at the appropriate operation time of the light irradiation and of the solvent extraction without light irradiation.

Table 6 Results of extraction operation after photochemical valence adjustment for coextraction of Pu and Np

(a) Abundances of Pu valences in both phases vs. operation time

Valence	Abundance(%)						
	Photochemical val. adj. time				Solv. ext. time		
	0 min	10 min	15 min	20 min	10 min	20 min	
Aq.	Pu(III)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Pu(IV)	82.3	65.3	58.9	53.2	3.5	3.6
	Pu(VI)	17.7	34.7	41.1	46.8	7.9	8.1
Org.	Pu(III)					<0.1	<0.1
	Pu(IV)			-		36.1	36.8
	Pu(VI)					52.5	51.5
Gross Pu in Org.						88.6	88.3
in Aq.						11.4	11.7
Org. / Aq.						7.77	7.55

(b) Abundances of Np valences in both phases vs. operation time

Valence	Abundance(%)						
	Photochemical val. adj. time				Solv. ext. time		
	0 min	10 min	15 min	20 min	10 min	20 min	
Aq.	Np(IV)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Np(V)	100.0	7.0	0.3	<0.1	7.7	7.7
	Np(VI)	<0.1	93.0	99.7	100.0	<0.1	<0.1
Org.	Np(IV)					<0.1	<0.1
	Np(V)			-		<0.1	<0.1
	Np(VI)					92.3	92.3
Gross Np in Org.						92.3	92.3
in Aq.						7.7	7.7
Org. / Aq.						12.0	12.0

Pu : 1.0×10⁻³ M
 Np : 1.0×10⁻³ M
 Urea : 1.0×10⁻² M

HNO₃ : 3.0M
 Temp. : 20°C
 Irra. rate : 1.45 W/cm²

As seen in this table, Pu(IV) was gradually photooxidized to Pu(VI) and nearly 100 % of the Np(V) was photooxidized to Np(VI) after 20 mins. On the other hand, during the extraction operation, 92.3 % of Np was extracted in the organic phase, and 7.7 % of Np remained in the aqueous phase after 10 mins. The Np valence remaining in the aqueous phase was Np(V), in spite of the complete adjustment to 100 % of Np(VI) being achieved. This indicates that part(about 8 %) of Np photooxidized to about 100 % of Np(VI) was reduced to Np(V) during the mixing operation with 30 % TBP/n-dodecane. The remaining Np(V) in the aqueous phase would be completely extracted into the organic phase by the recycling operation of the photochemical oxidation and the extraction.

Based on these data, it was shown that Pu and Np in a nitric acid solution were efficiently coextracted in 30 % TBP/n-dodecane using this photochemical technique.

2. Simultaneous operation for coextraction

A simultaneous operation test of light irradiation and solvent extraction for the coextraction of Pu and Np was carried out using a Pu and Np mixed solution containing urea. The results of this test are shown in Table 7.

Table 7 Results of simultaneous operation of irradiation and solvent extraction for coextraction of Pu and Np

(a) Abundances of Pu valences in both phases vs. operation time

	Valence	Abundance (%)			
		Just before operation	Time of simultaneous ope. of irra. and ext.		
			15min	30min	50min
Aq.	Pu(III)	<0.1	<0.1	<0.1	<0.1
	Pu(IV)	83.0	1.7	0.9	0.2
	Pu(VI)	17.0	9.1	9.7	10.0
Org.	Pu(III)		<0.1	<0.1	<0.1
	Pu(IV)	–	33.0	17.1	10.7
	Pu(VI)		56.2	72.3	79.1
Gross Pu in Org.		<0.1	89.2	89.4	89.8
in Aq.		100.0	10.8	10.6	10.2
Org./Aq.		–	8.26	8.43	8.86

Pu : 1.0×10^{-3} M
Np : 1.0×10^{-3} M
Urea : 1.0×10^{-2} M

HNO₃ : 2.0M
Temp. : 20°C
Irra. rate : 1.45 W/cm²

(a) Abundances of Np valences in both phases vs. operation time

	valence	Abundance (%)			
		Just before operation	Time of simultaneous ope. of irra. and ext.		
			15min	30min	50min
Aq.	Np(IV)	<0.1	<0.1	<0.1	<0.1
	Np(V)	100	97.2	99.3	100.0
	Np(VI)	<0.1	<0.1	<0.1	<0.1
Org.	Np(IV)		<0.1	<0.1	<0.1
	Np(V)	–	0.9	0.7	<0.1
	Np(VI)		1.9	<0.1	<0.1
Gross Np in Org.		<0.1	2.8	0.7	<0.1
in Aq.		100.0	97.2	99.3	100.0
Org./Aq.		–	0.03	0.007	<0.001

As seen in this table, the initial valences, Pu(IV) and Pu(VI), were extracted into the organic phase depending upon their specific distribution coefficients, and Pu(IV) in the organic phase decreased as Pu(VI) increased according to the irradiation time similar to the data shown in Tables 5-(a) and 7-(a). On the other hand, regarding Np, part of the Np(V) was photooxidized and was extracted into the organic phase. However, the extracted Np(VI) was gradually reduced to Np(V) and was then reversely extracted into the aqueous phase despite light irradiation. Therefore, Np(V) in the aqueous phase gradually increased. This result indicates that Np(V) was not photochemically oxidized to Np(VI) at all in the case of the simultaneous operation. It is quite different from the result shown in Table 6-(b) despite the same light irradiation.

This phenomenon also indicates that Pu and Np can be mutually separated using the Pu and Np mixed nitric acid solution containing not only HAN and HDZ but also urea in 3 M HNO₃ by the simultaneous operation of light irradiation and solvent extraction. This simultaneous operation is, however, not suitable for the purpose of the coextraction of Pu and Np with 30 % TBP/n-dodecane.

3.3 Photochemical dissolution

(1) Dissolution curve

Ten mg of UO₂ powder was placed in a quartz cell containing 2ml of a 3M HNO₃ solution. The solution was then irradiated using the Hg lamp at an irradiation rate of 1.3W/cm² while maintaining both the temperature of the solution (at 20 ± 1°C) and the homogeneity. Figure 7-(a) shows the results of the changes in the absorption spectrum of the solution according to the irradiation time. As shown in this figure, the absorption bands of UO₂²⁺ from 410 to 430nm and those of HNO₂ as a by-product of the UO₂ dissolution reaction from 360 to 390nm appeared after only 10 minutes of irradiation. These increases in the absorbances at these absorption bands show the increase in the dissolution fraction of UO₂ powder. Figure 7-(b) shows the changes in the UO₂ dissolution fractions which are calculated by Eq. (1) based on the data of Fig. 7-(a). The changes in the concentrations of HNO₂ according to the irradiation times are also shown in Fig.7-(b).

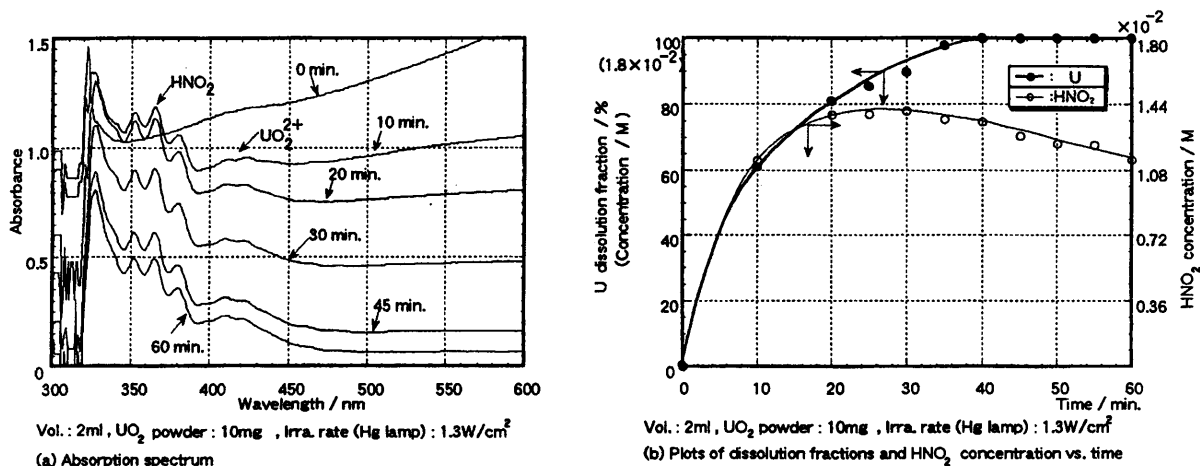


Fig.7 Photochemical dissolution of UO₂ powder in 3M HNO₃ solution at 20°C

As shown in this figure, the UO_2 powders were completely dissolved after 40 mins. of irradiation even at 20°C , with the same amount of HNO_2 as compared to that of the dissolved UO_2 powder which was produced after 15 mins. of irradiation. Then, after 30 mins. of irradiation, the amount gradually decreased.

Figure 8 shows the difference in the dissolution curves, the relationship between the UO_2 dissolution fraction and the irradiation time, for the different irradiation rates 0 (dark reaction), 0.7 and $1.3\text{W}/\text{cm}^2$. As shown in this figure, the photochemical dissolution reaction of 10 mg UO_2 powder at 20°C was completed at about 40 mins. and 80 mins. under the irradiation rates of 1.3 and $0.7\text{W}/\text{cm}^2$, respectively. Under the dark condition, the dissolution fraction was 45% after 90 mins. of irradiation.

Judging from these data, the irradiation rate significantly affects the photochemical dissolution reaction.

Figure 9 shows the results of the dissolution reaction of 10 mg UO_2 which were obtained with a $0.7\text{W}/\text{cm}^2$ irradiation rate at 20°C while varying the concentration of HNO_3 to 1, 3 and 6M.

The photochemical dissolution reaction in the 6M HNO_3 solution was completed after only 14 mins. at a $0.7\text{W}/\text{cm}^2$ irradiation rate. The complete dissolution time is about 1/5 of that in 3M HNO_3 solution. As for the 1M solution, the photochemical dissolution reaction hardly progressed, and the fraction being only 2-3% even after 90 mins. of irradiation.

The concentration of HNO_3 significantly affects the photochemical dissolution rate of UO_2 powder as seen above.

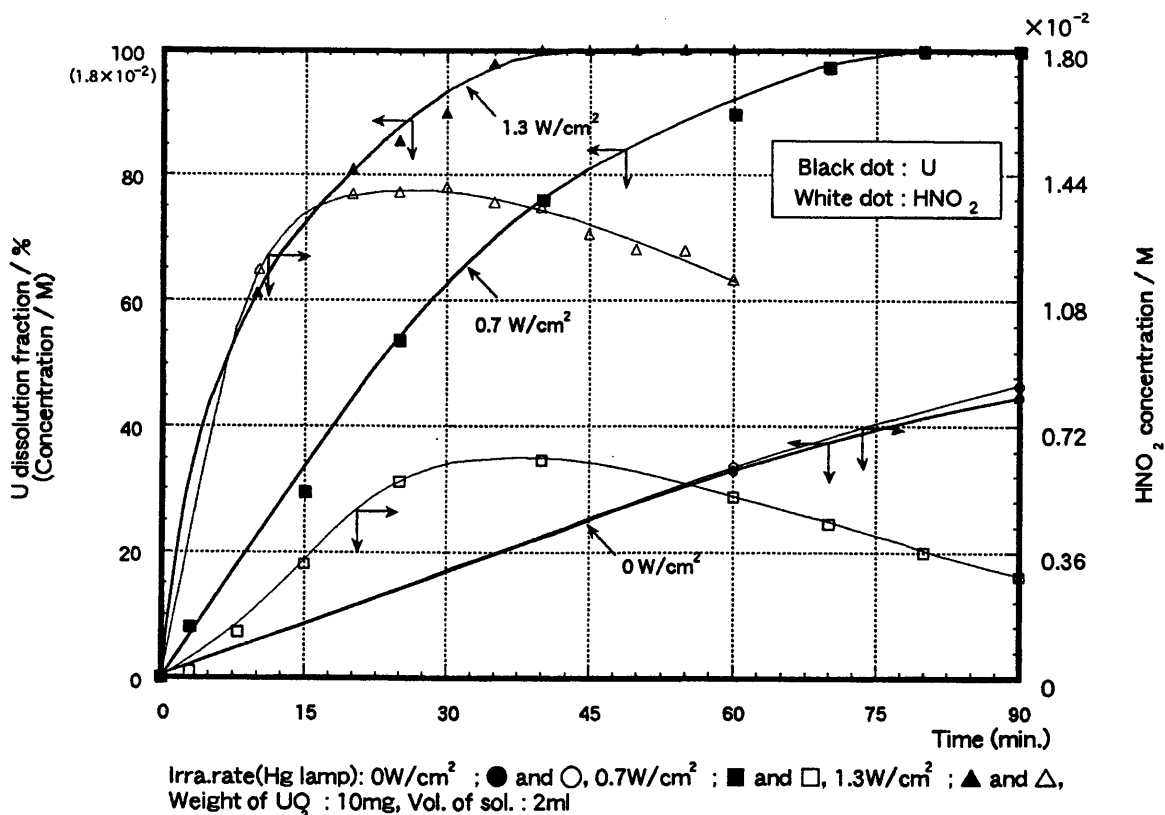


Fig.8 Photochemical dissolution of UO_2 powder in 3M HNO_3 solution at 20°C under various irradiation rates

Figure 10 shows the results of the photochemical dissolution reaction obtained by changing the weight of the dissolved UO_2 powder from 1, 10 and 100mg. As shown in this figure, the dissolution rate become faster in the order of 100, 10 and 1 mg, and the complete dissolution time become shorter in the same order

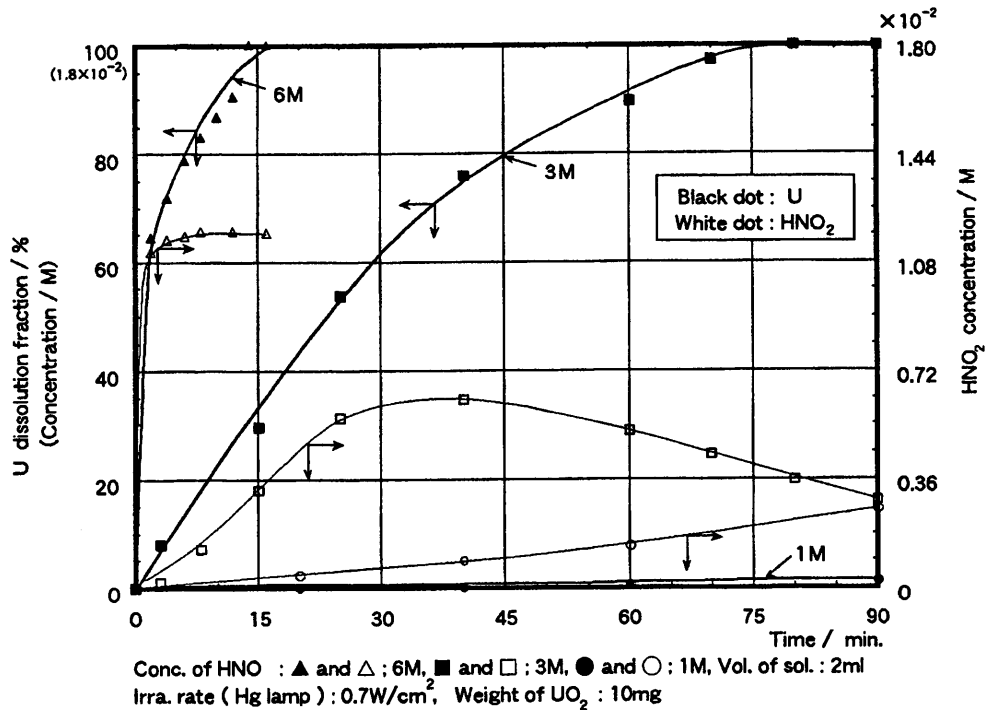


Fig.9 Photochemical dissolution of UO_2 powder in various concentration of HNO_3 at 20°C

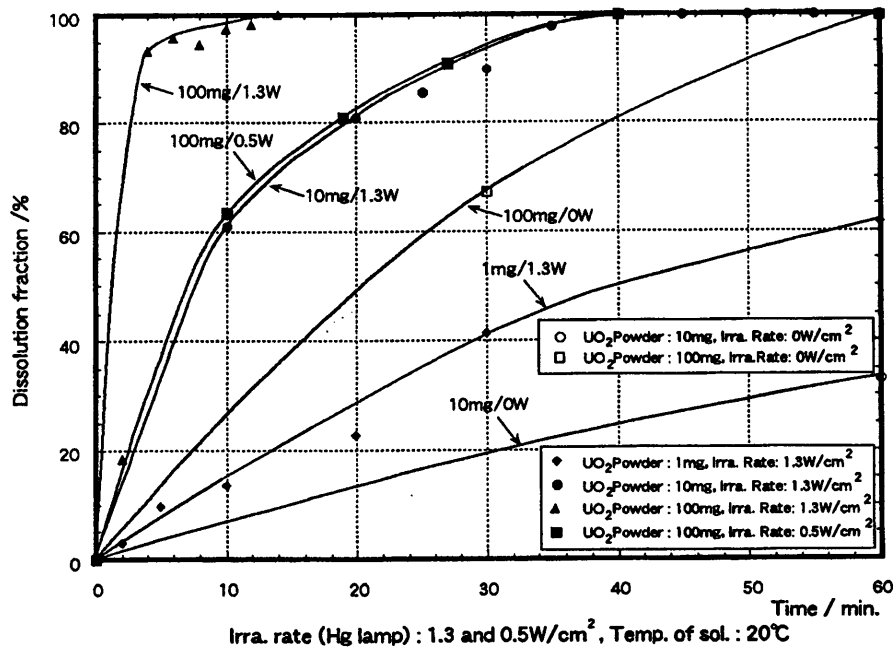


Fig.10 Photochemical dissolution of UO_2 powder 1mg, 10mg and 100mg in 2ml of 3M HNO_3 solution

(2) Photochemical dissolution reaction of UO_2 powder

The dissolution reaction mechanism of UO_2 powder in nitric acid solution has been studied by Y. IKEDA and H. TOMIYASU et al. (27) using a UO_2 powder enriched with ^{17}O . Additionally, X. MACHURON-MANDARD and C. MADIC (28) studied the dissolution reaction mechanism of PuO_2 powder using ^{18}O -enriched water. In these studies, they concluded that the UO_2 and PuO_2 powders were dissolved through a one or two electron transfer reaction based on the data from NMR analysis. These experiments indicate that the dissolution mechanism is by the redox reaction of electron transfer between a solvent such as nitric acid and UO_2 or PuO_2 powder.

Therefore, the standard electrode potentials are important in evaluating the dissolution reaction. The standard redox electrode potentials of nitric acid, nitrous acid, UO_2 , PuO_2 and related ion species based on several references (29), (30), (31) are shown in Fig.11.

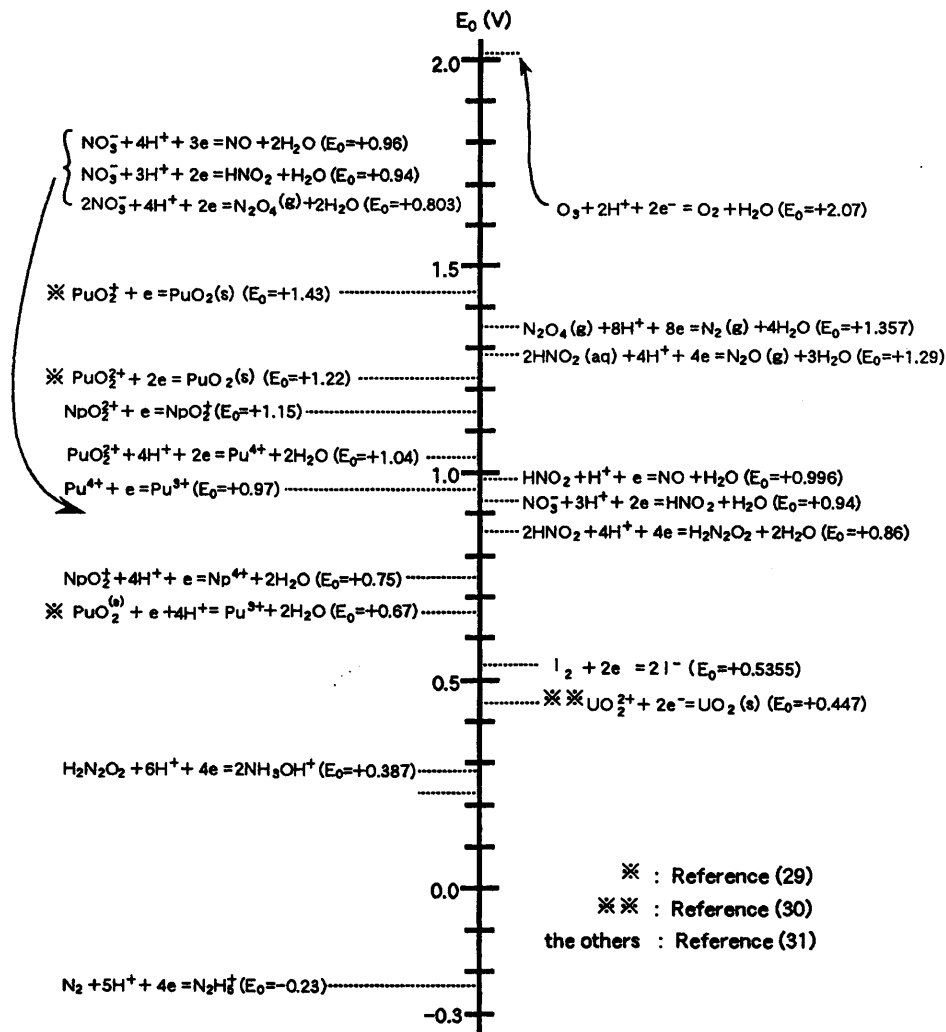
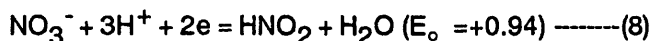
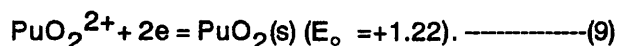


Fig.11 Standard redox electrode potentials of various reactions related to this study

In general, if the difference between two electrode potentials of a pair of half reactions, ΔE_0 , is larger than 0.4V, the redox reaction between the pair might easily progress. For example, in the case of the dissolution reaction of UO_2 in a nitric acid solution, the difference, ΔE_0 , between the two half redox reactions of NO_3^- and UO_2 is about 0.5V. Therefore, the reaction will easily progress. However, in the case of the dissolution reaction of PuO_2 in a nitric acid solution, the difference in the electrode potentials, ΔE_0 , is a negative value between these half reactions, Eqs.(8) and (9).

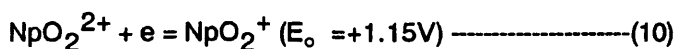


and

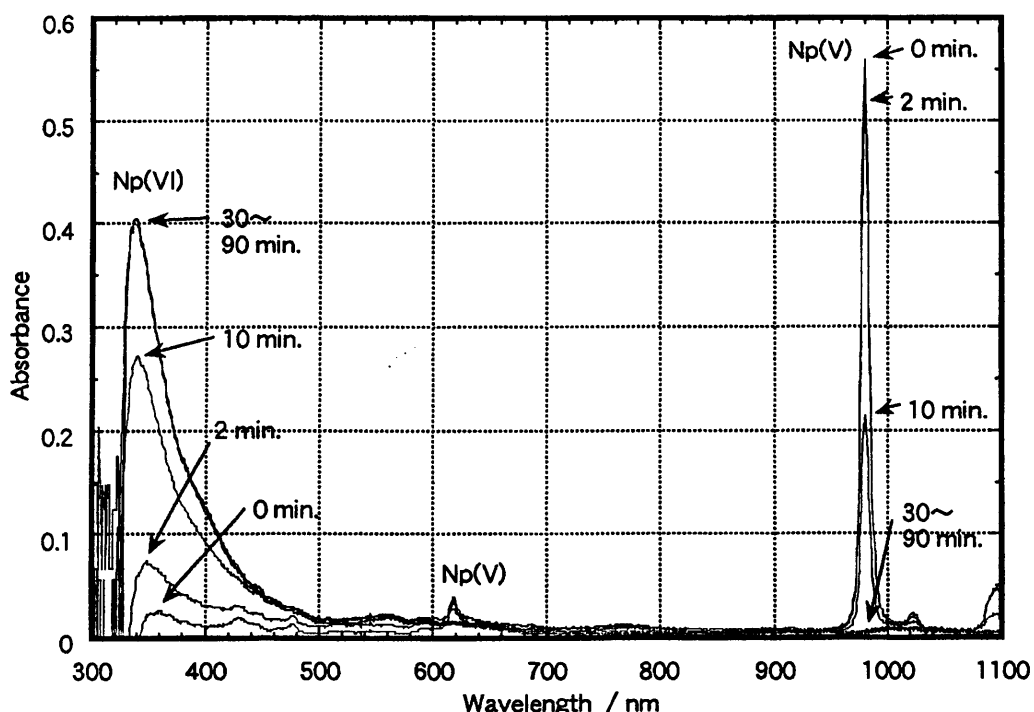


Therefore, in general, we have to heat the nitric acid solution to activate the potential of Eq. (8).

On the other hand, in the case of the oxidation reaction of Np(V) to Np(VI) by nitric acid ion, the difference between two of the half reactions, Eqs. (8) and (10) is also a negative value.



Therefore, the oxidation reaction of Np(V) to Np(VI) hardly progresses at room temperature in nitric acid solution. However, Figure 12 obtained in our previous study indicates that the oxidation reaction of Np(V) using the photochemical technique easily progresses. This oxidation reaction is thought to be caused by the photoexcited nitric acid ion, $^*\text{NO}_3^-$ (16), shown in Eq.(11) below.



Np : 1×10^{-3} M , Urea : 8×10^{-2} M , Acidity : 3.0M , Tem. of sol. : 20°C , Irra. rate : $1.45\text{W}/\text{cm}^2$, Irra. light wavelength : 250~600nm

Fig.12 Oxidation reaction of Np(V) to Np(VI) by photoexcited nitric acid

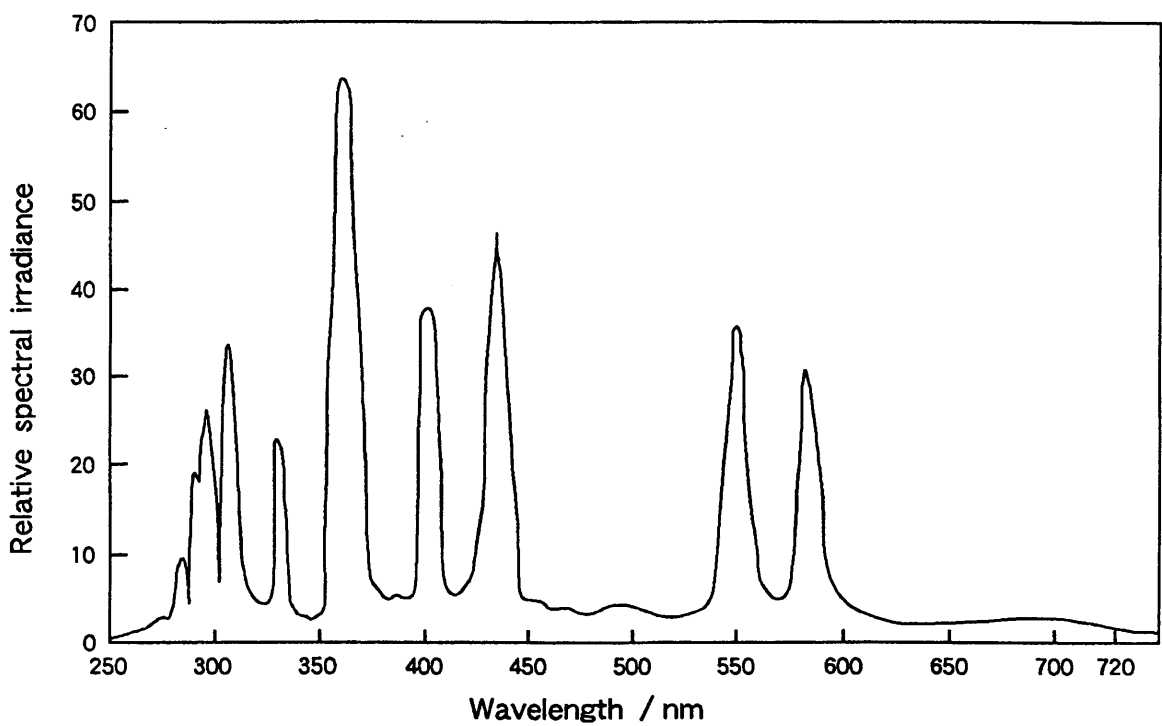


Fig.13 Relative spectral energy distribution curve of mercury lamp

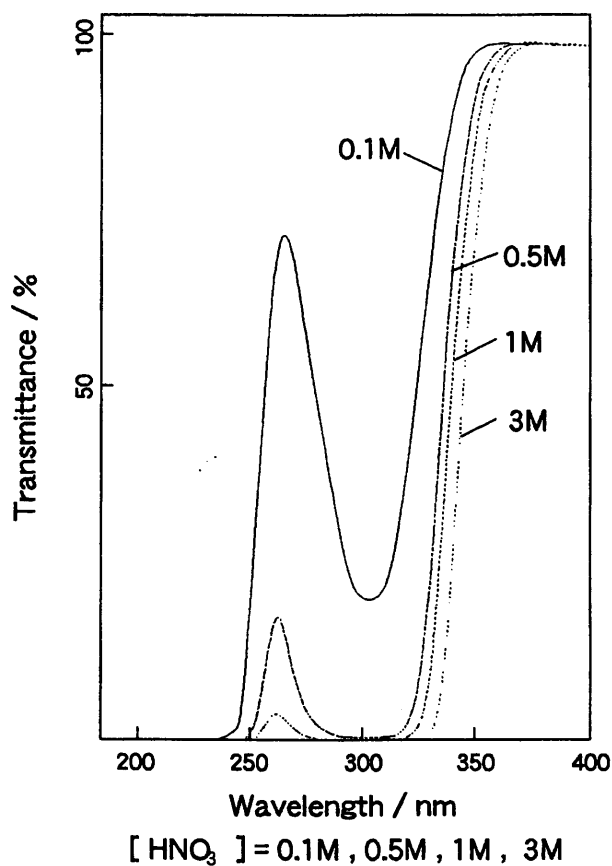
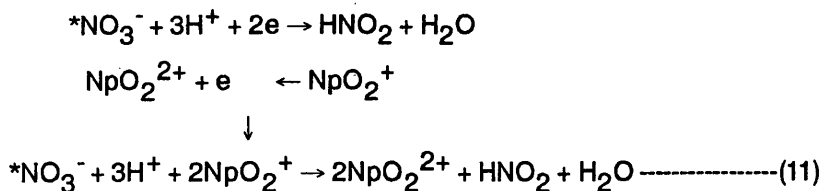


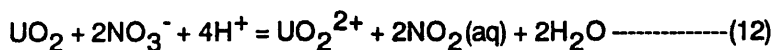
Fig.14 Absorption spectrum of HNO₃



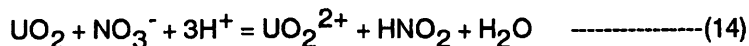
In general, a photoexcited species formed by the absorption of photon energy is more active and has a short-lived redox potential in proportion to the photon energy absorbed by the species⁽³²⁾.

Figure 13 shows the relative spectral energy distribution curve of the Hg lamp used in our study. Figure 14 shows the absorption spectrum of a HNO₃ solution from 0.1 to 3M HNO₃. Judging from both figures, it is ascertained that the Hg lamp light below 350nm photoexcites a nitric acid ion species, NO₃⁻. Based on the above-mentioned photoexcited nitric acid, *NO₃⁻, the results of the photochemical dissolution reaction of the UO₂ powder in nitric acid solution can be explained as follows.

Ikeda, Y. et al⁽²⁷⁾ explained the UO₂ dissolution reaction with nitric acid as follows:

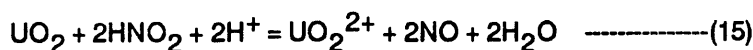


From Equations.(12) and (13), Eq.(14) is derived.

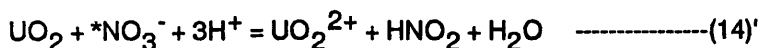


Equation (14) proves the production of UO₂²⁺ and HNO₂ as shown in Fig.1-(a).

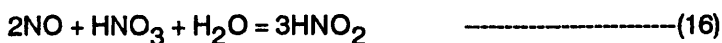
This nitrous acid then dissolves UO₂⁽³³⁾.



Under the Hg lamp irradiation, the irradiation rate and the concentration of nitric acid significantly affected for the dissolution rate. This is brought about by the increase in the concentration of the photoexcited nitric acid, [*NO₃⁻]. The dissolution reaction of the photoexcited nitric acid is shown in Eq.(14)' as related to Eq.(14).

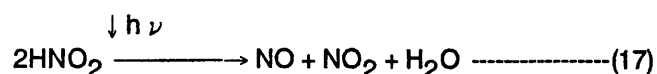


Nitrous acid is regenerated by the catalyzing reaction^{(33),(34)} after the dissolution reaction according to Eqs.(9) and (10).



As shown in Figure 7-(b), the concentration of the dissolved UO₂ and the generated HNO₂ were equal up to 20 mins. of irradiation time. This is due to the relationship among Eqs.(14)',(15) and (16).

Results similar to those of Fig.7-(b) were reported by T. Fukasawa et al. (35). After 20 mins. of irradiation time, the concentration of HNO_2 gradually decreases mainly due to the decomposition reaction of HNO_2 by the light as follows.



(3) Effect of irradiation rate on photochemical dissolution rate

Based on the results of Figures 8 and 10 obtained by the tests changing the variable level of the irradiation rate, the coefficient of the dissolution rates $V(\text{mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1})$ for 10mg UO_2 and 100mg UO_2 were calculated by the following Eq. (18) and are shown in Tables 8-(a) and -(b), respectively.

Table 8 Change in photochemical Dissolution rate depending on irradiation rate

(a) Weight of UO_2 : 10mg

Irra. rate (W/cm^2)	Disso. rate coef. ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$)	Ratio to dark rate coef.	Time for complete disso. (min)
1.3	3.50×10^{-6}	14.4	40
0.7	1.05×10^{-6}	4.3	78
0.0	2.43×10^{-7}	-	350

Acidity : 3M HNO_3 , Temp. of sol. : 20°C

(a) Weight of UO_2 : 100mg

Irra. rate (W/cm^2)	Disso. rate coef. ($\text{mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$)	Ratio to dark rate coef.	Time for complete disso. (min)
1.3	9.35×10^{-6}	8.9	14
0.5	3.00×10^{-6}	2.9	40
0.0	1.05×10^{-6}	-	60

Acidity : 3M HNO_3 , Temp of sol. : 20°C

$$V = \frac{\Delta D_0}{S_0 \times 10^4 \times w/1000} \quad \text{----- (18)}$$

where V : Coefficient of dissolution rate(mol · cm⁻² · min⁻¹)

ΔD₀ : Slope of dissolution curve obtained in tests at the beginning of

dissolution reaction(mol · min⁻¹)

S₀ : Specific surface area(m²/g) of UO₂ powder used in test shown in table 2

w : Weight of UO₂ powder used(mg).

In the case of 10mg UO₂, the ratio of the coefficients of the dissolution rate, V_{1.3} and V₀, and the complete dissolution times between the irradiation rates of 1.3W/cm² and 0W/cm²(dark) was 14.4 and 8.75, respectively. The ratio of the rate coefficients between V_{1.3} and V_{0.7} under 1.3W/cm² and 0.7W/cm² was 3.3, though the ratio of the irradiation rate was 1.9. In the case of 100mg of UO₂, the ratio of the coefficients of the dissolution rate between V_{1.3} and V₀ was 8.9. The ratio of the rate coefficients between V_{1.3} and V_{0.5} was 3.1 though the ratio of the irradiation rates was 2.6.

Thus, the increase in the irradiation rate of the Hg lamp significantly accelerated the photochemical dissolution rate of UO₂ powder in 2ml of a 3M HNO₃ solution at 20 °C, although the effect of the difference in the irradiation rate for 100mg of UO₂ dissolution was smaller than that for 10mg.

(4) Effect of concentration of HNO₃ on photochemical dissolution rate.

Based on the results of Figure 9, obtained by the tests changing the level of the HNO₃ concentration from 6M, 3M to 1M under an irradiation rate of 0.7W/cm², the coefficients of the photochemical dissolution rate were calculated and are shown in Table 9.

Table 9 Change in photochemical Dissolution rate depending on concentration of HNO₃

Conc. of HNO ₃ (M)	Disso. rate coef. (mol · cm ⁻² · min ⁻¹)	Ratio to dark rate coef.	Time for complete disso. (min)
6	4.20 × 10 ⁻⁵	3.0	14
3	1.05 × 10 ⁻⁶	4.3	75
1	1.17 × 10 ⁻⁸	-	-

Weight of UO₂ : 10mg, Irra. rate : 0.7W/cm², Temp. of sol. : 20, - : No mea.

As shown in this table, the ratio of the rate coefficients between 6M and 3M HNO₃ is 40.0 though the ratio of the acidity is only 2.0. The ratio of the rate coefficients between the photochemical dissolution reaction at 0.7W/cm² and the dark reaction under 6M HNO₃ is 3.0. The ratio of the coefficients of the photochemical dissolution rate at 6M and 1M HNO₃ is 3590. Thus, the effect of the concentration of HNO₃ on the photochemical dissolution reaction is clearly more significant than the effect of a change in the irradiation rate.

(5) Change in photochemical dissolution rate depending on weight of UO₂ dissolved

How much UO₂ powder can be photochemically dissolved in a definite volume of nitric acid solution is an important point for evaluating the applicability of this technology. Especially, as the penetration ability of the light is weak, and the transmittance of the Hg lamp light into the 1cm square spectrophotometric quartz cell containing 100mg UO₂ powder in 3M HNO₃ solution is only 1%.

At the beginning of this study, we doubted whether a weight of as much as 100mg of UO₂ powders can be photochemically dissolved in an amount as small as 2ml of 3M HNO₃ was in fact possible.

We, therefore, examined the photochemical dissolving ability by changing the weight of the UO₂ powder. Figure 10 shows the results when 1, 10 and 100mg of the UO₂ powder were photochemically dissolved in 2ml of 3M HNO₃ solution under the conditions of an irradiation rate of 1.3W/cm² and a solution temperature of 20°C.

Based on the results of Figure 10, each coefficient of the dissolution rate, the time for complete dissolution and the ratio of the rate coefficient to the dark reaction are shown in Table 10. As shown in this table, the dissolution rate for 100mg UO₂ in 2ml of 3M HNO₃ solution, which is a suspension rather like a concentrated mud solution, is the fastest of the three variable levels. The ratio of the coefficient of the dissolution rate between 100mg and 10mg UO₂ is 2.7.

Furthermore, the ratio of the time for the complete dissolution of 100 and 10 mg of UO₂ is 0.35.

Table 10 Change in photochemical Dissolution rate depending on weight of UO₂ powder dissolved

Weight of UO ₂ (mg)	Disso. rate coef. (mol · cm ⁻² · min ⁻¹)	Ratio to dark rate coef.	Time for complete disso. (min)
100	9.35 × 10 ⁻⁶	8.9	14
10	3.50 × 10 ⁻⁶	14.4	40
1	6.78 × 10 ⁻⁷	-	105

Irra. rate : 1.3W/cm², Acidity : 3M HNO₃, Temp. of sol. : 20, - : No mea.

Thus, in the range of 1 to 100 mg, it is concluded that the larger the amount of UO_2 powder, the faster the UO_2 powder dissolves. Although more detailed experiments and evaluations are required hereafter for more precise and quantitative estimations, the reasons for this phenomenon are considered nevertheless to be as follows:

- The larger the amount of UO_2 powder suspended in the nitric acid solution, the greater the probability of a collision between the photoexcited nitric acid species and the UO_2 powder is during the photoexciting state, the faster the UO_2 powder dissolves.
- The larger the amount of UO_2 powder suspended in the solution, the higher the concentration of nitrous acid generated due to the dissolution reaction is and also the faster the UO_2 is dissolved by the generated nitrous acid.
- The catalytic effect of UO_2^{2+} promotes the dissolution reaction of UO_2 powder^{(33), (36)}.

4. Conclusion

As advanced Purex technologies, separation and coextraction of Np from/with Pu in a mixed nitric acid solution and effective dissolution are needed in a new nuclear fuel cycle technology in the future.

The results of this study indicate that photochemical techniques for the separation and coextraction of Np from/with Pu, which involve the valence adjustment followed by solvent extraction, and the dissolution at room temperature have much potential for the above-mentioned purpose in principle.

References

1. Drake, V.A.: AERE-R-12761(1988)
2. Uchiyama, G., Fujii, S., Hotoku, S., Maeda, M.: RECOD '91 Proceedings Vol II , 723(1991).
3. Morita, T., Kubota, M.: JAERI-M-84-043(1984).
4. Palei, P. N., Nemodruk, A. A., Bezrogova, E. V. : Radiokhimiya, 11, 300(1969).
5. Bell, J. T., Friedman, H. A., : J. inorg. nucl. Chem., 38, 831-835(1976).
6. Friedman, H. A., Toth, L. M., Bell, J. T. : J. inorg. Nucl. Chem., 39, 123-126(1977).
7. Toth, L. M., Felker, L. K. : ORNL/TM-9958, (1986).
8. Park, Y. -Yu, Ikeda, Y., Harada, M., Tomiyasu, H. : Chem. Lett., 1329-1332(1991).
9. Nemodruk, A. A., Bezrogova, E. V., Ivanova, S. A., Novikov, Yu. P. : Zhu. Anali. Kihl., 27 [12] , 2414-2420(1972).
10. Friedman, H. A., Toth, L. M., Osborne, M. M. : J. inorg. nucl. Chem., 41, 1339-1345(1979).
11. Enokida, Y., Suzuki, A., : J. Nucl. Sci. tech., 26 [8] , 770-776(1989).
12. Uchiyama, G., Fujine, S., Hotoku, S., Maeda, M. : RECOD '91 Proceeding Vol. II , (1991).
13. De Poorter, G. L., Rofer-DePoorter, C. K. : LA-5630-MS Vol. II , (1976).
14. Gangwer, T. : BNL 50715, (1977).
15. Bell, J. T., Toth, L. M. : Radiochi. Acta, 25, (1978).
16. Wada, Y., Wada, K., Goibuchi, T., Tomiyasu, H., : J. Nucl. Sci. Tech., 31 [7] , 700(1994).
17. Wada, Y., Morimoto, K., Goibuchi, T., Tomiyasu, H.: Radiochi. Acta, 68, 233(1995).
18. Wada, Y., Morimoto, K., Goibuchi, T., Tomiyasu, H.: J. Nucl. Sci. Tech., 32 [10] , 1018 (1995).
19. Wada, Y., Morimoto, K., Tomiyasu, H. : Radiochi. Acta, 72, 195(1996).
20. Wada, Y., Morimoto, K., Tomiyasu, H. : Radiochi. Acta, 72, 83(1996).
21. Schulg, W. W., Burger, L. L., Nauratil, J. D. : "CRC Science and Technology of Tributyl Phosphate", Vol. III, CRC Press, Inc., Florida, 126(1990).
22. Tachimori, S.: J. Nucl. Sci. Tech., 28 [3] , 218(1991).
23. Vladimirova, M. V.: Radiochemistry, 36 [1] , 70-79(1994).
24. Biddle, P., Miles, J. H.: J. Inorg. Nucl. Chem., 30, 1292(1968).
25. Pogorelko, O. N., Ustinov, O. A.: Radiokhimiya, 35 [2] , 75(1993).
26. Koltunov, V. S., Frolov, K. M., Marchenko, V. L., Tikhonov, M. F., Zhuravleva, G. I., Kulikov, I. A., Ryabova, A. A.: Radiokhimiya, 24, 607(1982).
27. Ikeda, Y., Yasuike, Y., Takashima, Y., Park, Y-Yu., Asano, Y., Tomiyasu, H.: J. Nucl. Sci. Tech., 30 [9] , 962(1993).
28. Machuron-Mandard X., Madic, C.: J. Alloys Comp., 213/214, 100(1994).
29. Madic, C., Lecomte, M., Bourges, J., Koehly, G., Moulin, J. P.: RECOD'91 Proceeding Vol. II , 715(1991).
30. Bailar, J. C., Emeleus, H. J., SIR Ronald Nyholm, Trotman-Dickenson, A. F.: Comprehensive Inorganic Chemistry, Vol.5, 519(1973).
31. DeBethune, A. J., Lound, N. A. S.: Hampel Stokei, C. A., I 11, (1964).
32. Bock, C. K., Whitten, D. G., Meyer, T. J.: J. Am. Chem. Soc., 97, 2909(1975).

33. Taylor, R. F., Sharratt, E. W., de Chazal, L. E. M., Logsdail, D. H.: J. appl. Chem., 13, 32(1963).
34. Shabbir, M., Robins, R. G.: J. appl. Chem., 18, 129(1968).
35. Fukasawa, T., Ozawa, Y., Kawamura, F.: Nucl. Tech., 94, 108(1991).
36. Koga, J., Honma, S., Kanehira, O., Matumoto, S., Goto, M., Yasu, T., Kawata, T.: RECOD'91 Proceeding Vol. II, 687(1991).

Summary of Session 1

Co-Chairman: Dr. T. Mukaiyama

Professor Y. Fuji-ie, Commissioner of the Atomic Energy Commission (AEC), welcomed the participants. During his welcome address, he stressed the important role of nuclear energy for the future, and highlighted the Japanese position in carrying forward R&D efforts towards commercial implementation of the nuclear fuel cycle. One of the most important tasks for the mature nuclear fuel cycle, he said, was the establishment of the HLW management scheme. He noted that P&T type of work should continue at all times, because policy changes may occur in the future, and because basic research had rather long lead times. Such basic studies may provide insight into better and novel methods in solving HLW problems.

Mr. G. Stevens, Head of the Nuclear Development Division of the OECD Nuclear Energy Agency (NEA), opened the meeting and welcomed the participants on behalf of the NEA. He summarised the history of the NEA P&T programme and explained how it stimulated international collaborations for better understanding of the technical issues involved, and better orientation of future work. He was very pleased to see that so many participants from all around the globe were able to participate in the meeting and underlined that substantial benefits could be achieved from wider international co-operation. He thanked the Japanese Government for the generous support it provided in this field.

Mr. T. Arimoto, Director of the Radioactive Waste Policy Division, Science and Technology Agency (STA) of Japan, described the important position of geological disposal of HLW in the "Long-Term Programme for R&D, and Utilization of Nuclear Energy" issued by the AEC of Japan in 1994. In 1995, the AEC set up two committees for addressing the disposal of HLW, and the policy for the back-end of the nuclear fuel cycle. A wide range of studies for obtaining public understanding and for approving the implementation of HLW disposal would be performed. Other studies would consider technological issues concerning disposal. P&T was considered to be a future technology in the Long-Term Programme.

Mr. M. Hugon, European Commission (EC), reported on the EC-funded research activities on new fuel cycle concepts. These included three work areas, namely: strategic studies; partitioning techniques; and transmutation techniques. The strategic studies covered four projects: evaluation of possible P&T strategies; nuclear data for advanced MOX fuels; thorium cycles as nuclear waste management options; and impacts of accelerator-based technologies on nuclear fission safety. Experimental work on partitioning was carried out under two projects: new partitioning technologies, and extraction and selective separation of long-lived nuclides by functionalised macrocycles. Transmutation techniques studies were covered under two projects: the joint EFTTRA experiment on Am transmutation, with irradiation experiments performed in the HFR at Petten, and neutron driven transmutation by adiabatic resonance crossing. About forty European research institutions had participated to the projects since 1996, aiming at having a clearer picture in efficiently reducing the radiotoxicity of nuclear wastes.

Dr. A. Grigoriev, IAEA, reported on the IAEA activity on partitioning and transmutation. The IAEA first started a Co-ordinated Research Programme (CRP) in 1976 and its results were published in 1982. The conclusion of that report was rather negative for P&T. In 1990, the former Soviet Union requested the IAEA to re-activate its P&T programme. Since then, the IAEA organized two consultant meetings and one technical committee meeting on this subject. The IAEA had also initiated two CRPs, one on the safety, environmental and non-proliferation aspects of P&T, and another on benchmark calculations of a PWR-cell loaded with (Pu-Th) O_2 fuel and Th-cycle accelerator-driven systems. Two status reports

were in preparation, one on transmutation activities in non-OECD countries, and another on accelerator-driven hybrid systems. These IAEA activities which were complementary to other international programmes, especially to those of the OECD/NEA, were not expected to address possible proliferation issues regarding partitioning.

Mr. J.-F. Babelot of the JRC ITU reported on the EFTTRA irradiation experiments in Phenix and in the HFR. The objective of the European collaboration for Experimental Feasibility of Targets for Transmutation was conducting joint experiments for studying various materials for transmutation. Tc metal rods were irradiated in the HFR up to 6.4 per cent burn-up, and no swelling of the rods was observed. Based on the examination of the irradiated iodine containing capsules, NaI was concluded to be better than CeI_3 or PbI_3 . Inert matrices, namely oxide and nitride, were evaluated for MA transmutation both in a PWR and in a fast reactor, and the irradiation behaviour experiments of the candidate matrices were planned. The irradiation of Am oxide embedded in a spinel matrix was under preparation.

The international meetings organized by the NEA and the IAEA for exchange of information were seen as one of the most effective ways in obtaining a clearer picture of P&T aspects, which were both technically very complex and politically sensitive.

In Europe, as was reported by Messrs. Hugon and Babelot, well oriented and well organized collaborative P&T studies, including strategic studies, evaluations and experiments, were performed. The experimental data obtained by those joint efforts, especially irradiation data, would be very valuable for the international community in performing future work.

Following the introductory remarks and the reports on international activities, two invited key-note presentations were made: one by Dr. L. H. Baestle of SCK-CEN on a systems analysis approach for P&T issues and another by Professor M. Salvatores of CEA on the physics and strategies of transmutation.

Dr. Baestle was the Chairman of the NEA Expert Group on P&T System Studies which was preparing a report on that subject. His presentation focused on the general scope and the work of the NEA expert group. Professor Salvatores discussed the reactor physics approach for comparing different transmutation systems, namely, a fast reactor, a PWR, an accelerator-driven system, heterogeneous recycling and homogenous recycling. One of the conclusions of his analysis was that transmutation in PWRs was less attractive, and therefore, the role of Superphenix was very important for the development of targets for Am irradiation.

Summary of Session 2

Chairman: Professor M. Salvatores

In session 2, mostly national programmes had been presented (in Japan: the JAERI and PNC programmes; the activities in the Netherlands; the IPPE and ITEP activities in Russia; and in France the national programme and related scenarios studies).

In Japan, the framework was provided by the Long-Term Programme for Research, Development and Utilisation of Nuclear Energy. A new initiative had been taken by JAERI -- the Neutron Science Project. Accelerator-based transmutation was part (or would be part) of this project. In France, the framework was the 1991 Parliament Law for radioactive waste management, which required that work was performed during a fifteen year period, in order to gather the necessary elements for selecting appropriate options by the year 2006. In Russia, the role of the ISTC had been mentioned, since certain major programmes were performed there under funding of that Institute. Basic physics activities had also been highlighted.

The "double strata" concept by JAERI (presented by Dr. Mukaiyama) had the merit of conceptually confining the new P&T technologies to some specialised installations. This seemed to be a worthwhile approach to be further studied. In a somewhat opposite attitude (but also very valuable), the PNC approach (presented by Dr. Nakajima) favoured the optimisation of the standard fuel and fuel cycle technology, in order to reduce costs and increase competitiveness.

The French programmes (presented by Mrs Viala) illustrated priorities, in chemistry, for assessing, at the industrial level, the separation capability of trivalent actinides/lanthanides and, in fuel fabrication (Am targets), for realistic scenarios assessment.

In the scenarios presented by the CEA, MA were recycled in a fast reactor core: homogeneous recycling was preferred for Np, while heterogeneous recycling, by means of targets, was preferred for Am, in particular in a once-through option (this "hybrid" mode of recycling had also been considered by PNC in Japan).

The relevance of plutonium recycling characteristics was highlighted, both in the presentation of Dr. Rabotnov and in that of Dr. Delpech. In particular, the latter presentation gave quantified indications of mass flows in a reactor park recycling both plutonium and MA, and the related needs in fuel fabrication and fuel reprocessing plants; and this was a matter for discussion during the session.

From the presentations, it had been possible to recognise the wide network of international collaborations in all the fields of P&T (chemistry, physics, accelerator-based technologies). A significant example was the presentation of the Dutch programme by Mr. Kloosterman. Their programme was deeply embedded in European Commission activities and benefited from them.

In summary, constant progress had been reported by the major laboratories involved in the field. Perspectives seemed to be based on a relatively constant funding for these laboratories. The major challenge was still finding an appropriate measure for cost/benefit analyses.

Summary of Session 3

Chairman: Dr. P. Wydler

The contributions to this session covered studies of different transmutation systems (PNC, JAERI, KAERI), investigations relating to the P&T fuel cycle (JAERI, Belgonucléaire/EdF), and a target irradiation experiment with Tc-99 carried out in the Petten thermal High Flux Reactor (HFR) in the framework of the EFTTRA co-operation. Most of the important issues and options were addressed in the session including critical and accelerator-driven fast reactors with different types of fuel (oxide, nitride, molten salt) and wet or pyrometallurgical reprocessing, as well as different recycling modes (homogeneous, heterogeneous with inert matrices).

An option which relied primarily on proven reactor technology was to recycle the nuclides to be transmuted in a normal fast reactor. A comparison of different recycling modes for MAs and Tc-99 in a fast reactor was presented by PNC. Relatively high transmutation rates were reported for a case where Np was dispersed homogeneously in the core and Am, Cm and rare earths were recycled heterogeneously in target subassemblies in the blanket region. However, to preserve the safety characteristics of the core, the fraction of MAs in the fuel had to be restricted to about 5 wt%. For the transmutation of Tc-99 a new target subassembly concept using "duplex pellets" with zirconium hydride moderator was proposed.

Accelerator-based systems had the advantage that the deterioration of the core safety characteristics with increased MA concentrations can be compensated by the subcriticality of the core. Three accelerator-based systems for burning MAs were mentioned. In the framework of the OMEGA programme, JAERI investigates a solid system based on fast reactor technology (nitride fuel / sodium coolant) as also a "fast" molten salt system (molten chloride target / fuel) as a more advanced option, both systems being optimised for a high support ratio in the double stratum fuel cycle. An overview of the systems and the supporting R&D was presented, and a lead-based chloride salt was proposed as an alternative fuel for the molten salt system. The system studied by KAERI incorporated features of the Los Alamos ATW system (lead target, molten fluoride salt) and had an intermediate neutron spectrum in the core. A graphite reflector with a softer neutron spectrum was provided, but was found to be unsuitable for burning FPs at an interesting rate.

The current R&D status for the nitride fuel cycle at JAERI was summarised in an overview paper. Pellet-type mixed nitride fuel, fabricated by a conventional route, had been characterised and irradiation-tested in JMTR to a burnup of more than 5 per cent FIMA with good results (no pin failures, low FP releases), an alternative fabrication route for nitride fuel particles by the sol-gel method had been investigated, and the pyroprocess for reprocessing the fuel had been further evaluated; reprocessing experiments with NpN and PuN using laboratory-scale electrorefiners were about to begin.

The fabrication of target pins for the heterogeneous recycling of Am would be associated with higher radiation levels than the current MOX fabrication. In a joint study, Belgonucléaire and EdF had estimated the resulting dose rate increases and impact on the shielding for the different fabrication stages. Dose rate increases up to a factor of 2800 in the case of a transfer canister were predicted. Validation experiments were performed to assess the uncertainties of the calculations.

The EFTTRA co-operation aimed to investigate the behaviour of MA and FP targets during irradiation experimentally. In an irradiation of six metallic Tc-99 rods in the Petten HFR, more than 6 per cent of the Tc-99 was transmuted to stable Ru-100. ECN Petten performed the PIE for one of these rods and obtained reasonable agreement between measured and predicted ruthenium profiles provided that a Monte Carlo code with a point cross-section library was used in the analysis. A new measurement of the thermal absorption cross section of Tc-99 in the HFR may help to resolve remaining small discrepancies.

Regarding the evolution of the reported activities since the Cadarache P&T meeting in 1994, one could notice a move from the innovative to a stable development phase. Efforts in the fuel and target development area had been strengthened, and the concept of the double stratum fuel cycle, including accelerator-based MA burners, had found wider acceptance. Evaluations of the radioprotection implications had been initiated and filled an important gap. Considering the still not very clear incentive and goals for transmuting the fission products, the analytical and experimental effort devoted to studies of the Tc-99 transmutation was noticeable.

Summary of Session 4

Chairman: Dr. L.H. Baetslé

Considering the overall perspective for P&T, the first task to be tackled was partitioning, because otherwise transmutation would be an unrealistic endeavour. Partitioning was seen as an extension of the closed fuel cycle to those nuclides which constitute a potential and/or an intrinsic hazard. The obvious starting point of partitioning was the source term, where hazardous and long-lived nuclides were brought together with less toxic and short-lived nuclides; and that was the high-level waste solution.

If an analysis was attempted from that view point, methods which had been developed especially for that purpose should be considered. Three papers dealt with that subject directly:

- Products and wastes from 4-group partitioning process developed in JAERI (DIDPA process), by M. Kubota and Y. Morita of JAERI.
- Minor actinide separations: recent advances at the CEA (DIAMEX process), by A. Leudet, B. Boullis, C. Madic of CEA.
- The state of the art on nuclides separation in HLLW by TRUEX process, by M. Ozawa, Y. Koma, Y. Tanaka and S. Shikakura of PNC.

These methods were already under development during the previous NEA information exchange meeting. The highlights of these papers were as follows:

For the JAERI DIDPA process, the flowsheet was fully integrated and was capable of partitioning the HLLW nuclides into the following groups:

- TRU group
 - Am-Cm
 - Lanthanides
 - Np-Pu
 - U
- Platinum group metals (PGM) and Tc
- Cs-Sr

The process had only one drawback, that was the HLLW had to be partially de-acidified. Impressive separation and recovery yields had been reported (99.9, 99.5). The process produces only moderate amounts of secondary wastes (128 kg NaNO₃/tHM).

The DIAMEX process (CEA), permitted the quantitative extraction of MA from HLLW by the use of malonanide molecules (DMDBTDMA). However, continuous progress had been reported in the synthesis of new extractants with even better properties. The separation of An-Ln had not yet been demonstrated unequivocally and further progress was needed, but the prospects were good that a fully "saltfree -- high acid" process would become operational.

Concerning the TRUEX process (PNC), the flowsheet was a solid improvement of the original ANL flowsheet, since a number of "salt free" re-agents had been introduced and were successful. The flowsheet looked complicated but was, in fact, an integrated series of liquid extraction and strip operations providing: An-Ln fraction; plutonium; and Mo-Zr-Ru (contaminants recycled).

A major point to be noted was the direct use of HLLW solutions without dilution or de-acidification.

Closely associated with these "encompassing" partitioning methods, some very specific advances had been reported:

- Selective extraction and transport of cesium with CALI[4]ARENES crown CRWN from radioactive liquid wastes, by J.F. Dozol et al. from CEA.

These new molecules, with very complex structure, were capable of extracting selectively Cs-137 from a variety of active solutions, including HLLW. Currently, the kinetics were slow, but progress may be expected (contact phase, temperature, etc.):

- Partitioning of minor actinides from rare earths by solvent extraction with D 2 EHPA, by J.-H. Yoo et al.

This technologic development was a necessary step in the mastering of more elaborate partitioning methods.

A very special type of partitioning technique was the pyrometallurgical partitioning approach. This technology needed to be considered as a step in the future, when very highly irradiated targets and fuels would be produced in fast reactors and, possibly, in ADT facilities, to the extent that multi-recycling of such targets was required. Three papers from CRIEPI and associates dealt with this subject:

- Molten salt electrorefining to separate TRUs from rare earth elements, by T. Hijikata et al.
- Pyrometallurgical processing technology development, by T. Koyama et al.
- Development of pyrometallurgical partitioning technology of long-lived nuclides -- development of salt wastes treatment technology, by Y. Sakamura et al.

Pyrometallurgical techniques were difficult to implement, because of the "moisture" and, sometimes, the "oxygen" interference in the processes. But they had a fundamental merit that radiation damage and decay heat emission did not play a significant role, and that criticality risks were minimal.

The technological requirements were, however, much more severe than those for aqueous methods:

- HLLW must be denitrated and chlorinated.
- Electrochemical processes were complex.
- Separation factors were, generally, smaller.
- An important technological effort had been accomplished in the electrorefining, but much needed still to be done.
- Waste issues had been studied -- in particular, how to treat unrecyclable residues (NaCl, Cd, etc.). Questions regarding immobilization processes of salt residues were given tentatively acceptable answers (sodalite solidification of NaCl; Pb-Cd embedment).

In summary, great technological efforts needed to be made in order to consider pyrometallurgy as a viable option for multi-recycling of fuel and target materials.

An overview was also provided, by I.V. Mukhin, of the R&D work going on in Russia in the partitioning field. This would certainly lead to improve contacts with Russian colleagues.

Concerning international co-operation, task distribution should be performed according to available means and resources in order to avoid duplication. It would be worth trying to recontact colleagues in the United states to resume collaboration.

The future tasks could be summarised as follows:

- Investigate the link between spent LWR-MOX and P&T operations.
- Bridge the gap between the waste management and P&T communities.
- Further investigate the recycling technologies of very hot fuels and targets. Study the limits of the aqueous processing.
- Start performing strategic studies of P&T in the general context of nuclear development.

Summary of Session 5A

Chairman: Dr. J. Kloosterman (Netherlands)

In this session, posters were presented with a large variety of subjects and scopes ranging from short-term to long-term research.

The presentation started with the poster of Dr. Emoto (PNC) about the status of the electron accelerator, which could be used to transmute radioactive fission products with a small neutron capture cross section. Possible candidates of such fission products were Sr-90 and Cs-137.

The next three posters by Drs. Kusano, Nishida and Takada gave a coherent overview of work done at JAERI on Accelerator Driven Systems. The second poster dealt with the status of the R&D on the proton linac with energy of 1.5 GeV and an average current of 5 mA. This was already a big step towards an accelerator with a current of 40 mA needed for ADS. The third poster focused on the improvement and benchmarking of the NMTC cascade code and its inclusion in the ATRAS code system. This code can now be used to model the spallation reaction and high-energy fission processes, the neutron transport, and the core burn-up. It had been used to design two types of reactor systems: a nitride-fueled reactor for the short term and a molten salt fueled reactor for the longer term. Both systems were capable of transmuting the minor actinide production of ten units of 1 GWe LWRs. The benchmarking of the new ATRAS code system with experimental data was described in the fourth poster of this session by Dr. Takada.

Some interesting measurements were presented in the fifth and sixth poster presentations by Dr. Harada of PNC and Dr. Oigawa of JAERI. In the fifth poster, the measurements of thermal cross sections and resonance integrals of some important fission products were described. Interestingly, the cross section of Tc-99 was much larger than that assumed until now. For Sr-90 and Cs-137, the measurement of the photonuclear cross sections was in progress. In the sixth poster, the neutron fission yields and the delayed neutron data of some minor actinides were presented. Both fields were very important for the future development of burner reactors loaded with large amounts of minor actinides and fission products.

The last two posters dealt with the development of nitride fuels for future fast reactors. In the seventh poster, by Y. Arai, the lattice parameter, vapour pressure and thermal conductivity were presented for solid solutions of neptunium-plutonium mixed nitrides. Given that thermodynamic data on nitride compounds of minor actinides were not well known, that paper constituted a valuable contribution. Much work remained to be done, even on oxide compounds of minor actinides. The eighth paper, by M. Akabori, provided a better insight on nitride forming reactions in liquid alloys, which was of interest for the conversion of metallic fuels to nitrides.

In general, it was very positive that measurements of cross sections, neutron fission yields, and thermodynamic data had been performed, because the importance of such data cannot be easily underestimated. Also the validation and benchmarking of codes being used for new applications like accelerator driven systems were quite important. Future work on those subjects would further advance P&T research.

The non-technical aspects of the session concerned mainly the economics of accelerator driven systems. Since every stage of the nuclear fuel cycle was expected to become more expensive in the long term, the design of an accelerator driven system, which may consume up to 40 per cent of its own generated electricity, should be carefully investigated in order to make such systems as cheap as possible. Additionally, issues related to licensing should not be forgotten.

Summary of Session 5B

Chairman: Mr. M. Hugon

Five posters were presented by Japanese research institutions in this session. Three subjects were treated: (i) liquid-liquid extraction, by JAERI (two posters); (ii) dry reprocessing, by PNC (two posters); and (iii) photochemistry, by PNC (one poster).

JAERI presented the PARC (Partitioning Conundrum Key) process concept. This concept was developed by using the Back-End Cycle Key Elements Research Facility (BECKY) in NUCEF. Simplification of the chemical process and enhancement of the separation efficiency and of the confinement capability of long-lived nuclides were key parameters in improving economical competitiveness and safety standards.

The subject of the second poster was a presentation of the Partitioning Test Facility built in NUCEF in order to test the 4-group partitioning process developed by JAERI with real HLLW. Two to twenty liters of HLLW (5 000 Ci at maximum) can be treated during each experiment. Partitioning tests with simulated HLLW had already been started.

Recovery of valuable metals from spent nuclear fuel by lead extraction from high-level radioactive waste was investigated by PNC. Ruthenium was selectively separated by ozone oxidation. Different methods such as solvent extraction, precipitation and ion exchange were studied for the selective separation of rhodium and palladium. A process to recover technetium would be developed at a later stage.

A very high temperature method was being developed by PNC to separate platinum group metals from the actinide and rare earth elements. Titanium nitride was mixed with calcinated HLLW. The oxides of the platinum group elements were reduced into a metallic phase and partitioned from the oxide phase containing the actinides and rare earths at 1 600 degrees C.

In the last poster, PNC presented an application of photochemical techniques for the separation and co-extraction of neptunium from/with plutonium in a mixed nitric acid solution. The solution was irradiated by a high-pressure mercury lamp, which led to a valence adjustment of neptunium and plutonium, and, then, to a substantial improvement of their co-extraction in the organic phase. The photochemical dissolution of UO_2 powder in a nitric acid solution, at room temperature, appeared also to have much potential.

Summary of the Meeting

Mr. J. Lefèvre

Following the Mito City P&T Information Exchange meeting, related issues seemed to be better understood for the following reasons:

1. Goals were more clear:

- P&T would not replace geological disposal.
- Potential hazard reduction was mainly associated with TRU elements (Pu > Am >> Np, perhaps Cm).
- Reduction of the dose impact to man would come from mobile fission product radionuclides (I-129, Cs-135 > Tc-99).

2. The main motivations for P&T were:

- Ethical reasons for the future generations.
- Public claims concerning geological waste disposal sites (for example, in France).

3. There was, however, a need to better define the following:

- Performance to be coupled with which type of criteria (feasibility, credibility or safety gains) ?
- Which time limits should be considered (1 000, 10 000, 100 000 years or even more) ?
- Which were the best ways for industrial implementation (existing processes and facilities adaptation, new processes and new technologies or a step by step approach) ?
- What would constitute a reasonable level of extra costs ?
- Which were the safeguards aspects to be taken into account ?

Although P&T was seen as a rather long-term research programme, immediate and continuous answers were always needed by decision-makers and politicians. In this regard, it would be necessary: to continue performing technical studies; to continue evaluating the results obtained; to continue with systems and strategic studies; and to continue with the necessary economical evaluations.

Although several disparate approaches were under way, it should be recognised that two large programmes were currently leading P&T efforts: OMEGA in Japan and SPIN in France. Both were in good progress. Partitioning can be performed by both aqueous, and by dry and pyrometallurgical processes, while transmutation could be accomplished by reactor concepts (thermal and fast), fuels and targets, and by accelerators. Concerning partitioning and conditioning two new facilities were in operation: ATALANTE and NUCEF.

Given that P&T programmes constituted long-term activities, there was clearly a role for international organisations in order to disseminate results and ensure proper co-ordination of resources.

Session 6 (Closing Remarks)

Chairman: Mr. G.H. Stevens

It was very positive that so many knowledgeable people from all over the globe participated in the meeting. Warmest thanks were due to the organisers for having hosted an excellent meeting and for their hospitality.

Although some ideas presented were radical in the extreme, over the last few years more filtering of concepts was done and more experiments were performed. Issues concerning benefits for future generations vis-a-vis the risks for facility workers were becoming more prevalent.

Despite the widespread effects of privatisation and the introduction of greater competition into electricity production, resulting in reduction of energy R&D budgets, it was encouraging to see that stable funding was generally ensured for work on the P&T option.

The NEA would go ahead with its P&T systems studies activity and, given the ever increasing number of meetings in this area, would carefully evaluate the future continuation, scope and type of P&T Information Exchange meetings at appropriate intervals.

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