Modeling of Purex Process and Its Simulation

A Thesis
Presented to
Graduate School of Science and Engineering
Saitama University

Shunji HOMMA

March, 1995

ABSTRACT

The objective of this thesis is to contribute for design and operation of Purex process, which is adopted as commercial spent nuclear fuel reprocessing plant, by modeling of the Purex process and its simulation. The following studies were carried out in this thesis especially for the dissolution process in the head end process and the extraction process as the main process.

(i) Modeling of the dissolution dynamics and its simulation:
Rate equations developed here involve both penetration of nitric acid solution into the uranium dioxide pellet and chemical reaction kinetics. Rate constants in the equations were determined from several experimental results of the UO_2 pellet dissolution. Simulated results based on the rate equations gave good agreement with the experimental ones.

(ii) Modeling of the extraction process in the pulsed column and its simulation:
A progression model, which was able to describe axial change of back-mixing in the pulsed column and had simple expression, was adopted as the simulation model of the extraction process in the pulsed column. Both the steady-state and dynamic simulation of extraction behavior in the pulsed column gave good agreement with simulated experimental results.

(iii) Estimation of distribution coefficients of neptunium, uranium and plutonium in TBP/n-dodecane-nitric acid system:
The estimation equations of the distribution coefficients

of neptunium, uranium and plutonium in TBP/n-dodecane-nitric acid system were developed. Respective equilibrium constants in the equations were correlated with the total ionic strength in the aqueous phase. Distribution coefficients estimated by these equations gave good agreement with the experimental data presented.

(iv) Analysis of oxidation-reduction reaction between Np(V) and Np(VI) by nitrous acid and simulation of neptunium behavior in the extractor:
Rate and equilibrium constants of the oxidation-reduction reaction were determined from extraction experiments with mixer-settler based on a new extraction model, which had an assumption that all oxidation-reduction reactions occurred only in aqueous phase. By using determined rate equation, simulated neptunium concentration profiles in the mixer-settler gave good agreement with the experimental profiles.

(v) Development of Purex process flowsheet calculation system:
A COMPAS (COMputer aided Process flowsheet design and analysis system for nuclear fuel reprocessing) system was summarized. An example of the application was shown for the determination of operational conditions for flow control of neptunium in the Purex process. This system is available for R&D study on the safety operation and waste minimization of the Purex process.

TABLE FOR CONTENTS

IV. DISTRIBUTION COEFFICIENTS OF NEPTUNIUM AND OXIDATION-REDUCTION REACTIONS OF NEPTUNIUM 44

ACKNOWLEDGMENTS

Many persons have contributed either directly or indirectly to this thesis. I would like to thank them and to mention some of them.

I am greatly indebted to Professor Shiro Matsumoto and Associate Professor Jiro Koga, Department of Applied Chemistry, Saitama University, for their continuing guidance in all phase of this thesis work. I enjoyed working owing to their hearty encouragements.

I also thank Associate Professor Issei Iwamoto and Associate Professor Hidehiko Kobayashi, Department of Applied Chemistry, Saitama University, for their useful suggestions and advice.

Mr. Mitsuru Maeda, Head of Process Engineering Laboratory, Japan Atomic Energy Research Institute and Mr. Tomio Kawata, Head of Reprocessing Technology Development Division, Power Reactor and Nuclear Fuel Development Corporation of Japan, provided opportunities of the experiments in this thesis and gave me their useful advice. I am grateful to them.

In Chapter II, Mr. Takami Yasu, Manager of Components and Materials Development Section, and Mr. Minoru Goto, Engineer of Components and Materials Development Section, Power Reactor and Nuclear Fuel Development Corporation of Japan, took pains for the experiments, I should like to thank them.

In Chapter III, I would like to thank Dr. Sachio Fujine, Senior Research Engineer of Process Engineering Laboratory, Japan Atomic Energy Research Institute, for his useful suggestions.

In Chapter V, I also thank to Mr. Akio Togashi, General Manager of Process and Analysis Development Section, and Dr. Masaki Ozawa, Senior Stuff of Process and Analysis Development Section, Power Reactor and Nuclear Fuel Development Corporation of Japan, for their useful suggestions and advice.

Many colleagues and students have also contributed experiments, calculations and so on. They have also provided me with useful suggestions and advice. I am grateful to them all. Osamu Kanehira and Akihiko Nammo were helpful with the computational work in Chapter II when they were graduate students. Mr. Makio Watanabe was helpful with the experimental work in Chapter III when he was in Japan Atomic Energy Research Institute. Mitsuhiro Takanashi, Yuki Sato, Takahiro Miyo, Yoshihiro Satoh and Takayuki Soejima were helpful with the computational work in Chapter IV,·V and VI when they were graduate students. Susumu Sakamoto contributed the development of COMPAS and was helpful with various part of the computational works when they were graduate students. I offer them my thanks again.

CHAPTER I

INTRODUCTION

I-1. Modeling of Purex Process and Its Simulation

Spent fuel discharged from a nuclear power reactor after irradiation contains large amounts of radioactive and neutron-absorbing fission products. On the other hand, appreciable amount of valuable fissile nuclides, such as ^{235}U and plutonium are still contained in the fuel. Spent nuclear fuel reprocessing, therefore, is carried out in order to recover uranium and plutonium for reuse as the fuels and to remove the radioactive and neutron-absorbing fission products from them. Recovered uranium and plutonium can be recycled to a light water reactor (LWR) or a fast breeder reactor (FBR). Research and development of the fuel reprocessing are very important for the fuel cycle as well as those of the FBR and a uranium enrichment. Several commercial reprocessing plants have been constructed and operated in U.K. and France. In Japan, a large scale commercial reprocessing plant is building at Rokkasho-mura, Aomori prefecture and is going to be operated early in the 21th century. These plants have adopted the Purex process for enriched uranium fuel from the LWR power plant.

The Purex process was developed by General Electric Company (GE) in U.S. and carried out the first pilot-plant experiment at U.S. Oak Ridge National Laboratory (ORNL) from 1950 to 1952. Solvent extraction technique was used in the Purex process to separate uranium and plutonium from other nuclides. **Figure I-1** shows the schematic diagram of the Purex process[1]. The process consists of a series of three steps;

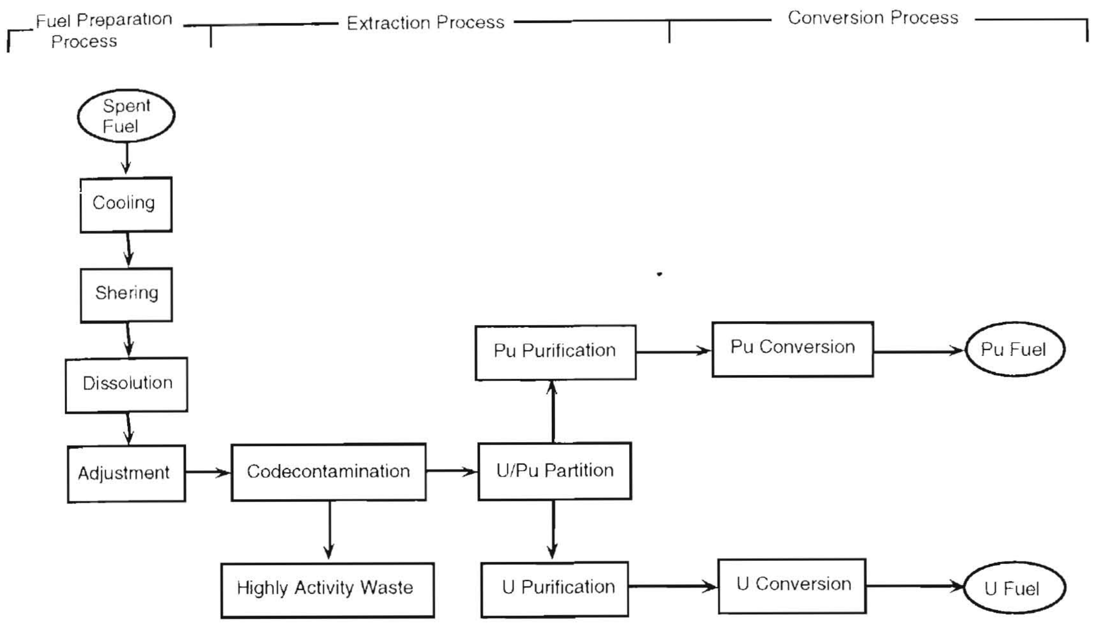

Fig.I-1 Schematic diagram of Purex process

preparation, extraction and conversion. The main purpose of the preparation step is to change the fuel rods shipped from the nuclear power plant from solid form to liquid one in order to carry out liquid-liquid extraction at the following step. After cooling the fuels in a water pool, they are sheared to a number of small pins mechanically. After that, the sheared pins are dissolved in a hot nitric acid solution. The dissolution, which contains uranium, plutonium and other fission products, is adjusted to proper concentration, then fed to the next extraction step. The extraction step consists of three parts; co-decontamination, U-Pu partition and the respective purification process. This step uses a mixture of tributyl phosphate (TBP) and a hydrocarbon diluent to extract uranyl nitrate and tetravalent plutonium nitrate from an aqueous solution containing nitric acid. In the co-decontamination process, the uranyl and the tetravalent plutonium nitrates are extracted by TBP to separate from other nuclides such as fission products (FP) and other transuranium (TRU) elements. Separation of plutonium from uranium is carried out in the following U-Pu partition process. This is done by reducing the plutonium from tetravalent state to the trivalent one, in which it is not extractable by TBP. Uranous nitrate ($U(NO_3)_4$) and hydroxylamine are generally used as the reducing agents of the tetravalent plutonium. The separated uranium and plutonium are purified by solvent extraction in the respective purification process. A mixer-settler, a pulsed column and a centrifugal contactor are used as extractor in the extraction step. After the extraction step, the purified uranium and plutonium nitrate are converted to oxide form, such as UO_2 and PuO_2, in the conversion step. The uranium and plutonium oxides are stored or shipped to a uranium enrichment facility or a fuel fabrication facility.

As stated above, the Purex process seems to be an established technology. However, there are still many problems that should be solved at present and in the future. The former research and development for the Purex process was aimed to effective separation of uranium and plutonium as the fuels. Recently, the large part of the problems, however, are concerned with safety aspect and radio active waste management.

It is needless to say that the safety operation of the Purex process has been achieved. If a Mixed Oxide Fuel (MOX) for the LWR or the FBR fuel is reprocessed by the Purex process in the near future, the operational conditions for a conventional uranium oxide fuel must be changed. It is also required more careful consideration for the safety operation prudently, because the irradiated MOX and FBR fuels should have more active fission products than the irradiated conventional uranium oxide fuels.

Before considering a reasonable radio active waste management, we should care about minimization of the waste volume from the reprocessing plant. Behavior of the uranium and plutonium in the Purex process has been almost known. In spite of containing various nuclides except uranium and plutonium in the waste, the behavior of the other nuclides, such as TRU elements and FP, however has not been made almost clear. Further researches for the characteristics of other nuclides are required for the waste minimization problems in the Purex process.

It is usual for their researches and developments to carry out experiments in a hot laboratory. Such the experiments are more danger than the experiments in a cold area. Moreover, it is very expensive and time-consuming because of shielding to radiations, disposal of experimental waste and so on. For these reasons, it is advisable for the researches and developments of the Purex process to simulate the nuclide's behavior in the process by a computer numerically as much as possible.

The important steps in the Purex process are the dissolution and the extraction. It is not too much to say that these two steps determine the behavior of the process. Therefore, modeling and simulation studies for the dissolution and the extraction process are illustrated in this thesis. From the viewpoint of numerical simulation, three characteristics of the process are given below;

(i) The process has heterogeneous system, solid-liquid and liquid-liquid system.

(ii) Reaction rates and equilibrium constants are described by non-linear functions depending upon the concentration of the components in the system.

(iii) A lot of nuclides must be handled by the numerical simulation in view of the safety and the waste minimization.

Review of the previous works about the numerical simulation for the Purex process is given in the next section.

I-2. Review of Previous Works

Modeling and simulation studies for the Purex process have been carried out for process design and its operation. A main concern in their studies was behavior of uranium and plutonium in the equipment, such as a dissolver and an extractor. The studies aimed an improvement of safety and a minimization of the waste, however, cannot be found too much at present. Review of previous works for modeling and simulation in the dissolution and the extraction process are described in the following sections. Previous works for the process flowsheet calculation of the Purex process are also described.

I-2-1. Dissolution Process

In the dissolution process, reaction kinetics of the dissolution have been studied experimentally. Taylor et al. have attempted to make a qualitative assessment of whether the process is controlled by chemical kinetics or by penetration of reacting species and the initial rate of dissolution has been attributed to the build-up of nitrite ions, which then catalyze further dissolution[2]. Shabbir et al. have attempted to allow for a changing surface area for dissolution by assuming that the dissolution occurs uniformly at the external surfaces of fuel pellets[3,4]. This approach, however, is only applicable to describe the initial dissolution rate. It is known that the fuel dissolution behavior strongly depends on the conditions of the fuel pin, e.g., conditions of sintering, irradiation and so on. These results imply that the fuel dissolution involves some complicated processes, such as penetration, reaction and so on. Hodgson has proposed a numerical simulation model to describe the complicated behavior of fuel dissolution[5]. He has also determined the penetration rate constants of his model. He, however, did not give the details of the chemical reaction kinetics.

I-2-2. Extraction Process

In the extraction process, several simulation programs, which are simply called "codes" or "simulation codes", have been developed since early 1970's. The codes simulate the extraction behavior of uranium, plutonium and nitric acid in the extractor. Since model descriptions of the mixer-settler and the pulsed column are different from each other, the code has independently developed for the each type of the extractor.

For the mixer-settler, typical simulation codes are SEPHIS[6] and MIXSET[7] developed at the ORNL and Power Reactor and Nuclear Fuel Development Corp.(PNC) in Japan, respectively. Equilibrium stage is applied to one stage of the mixer-settler for both the SEPHIS and the MIXSET. Estimation equations of distribution coefficients for uranium, plutonium and nitric acid are the functions of nitrate ion concentration in aqueous phase.

For the pulsed column, typical simulation codes are PULCO[8], DYNAC[9] and VISCO[1][10] developed by Gonda et al., Nabeshima et al. and Petrich et al., respectively. Since the pulsed column is operated by giving a continuous pulsation to achieve a uniform mixing, the flow in the pulsed column is not ideal, then the equilibrium stage model can not be applied. A dispersion model[11], therefore, was applied to the PULCO and the VISCO to describe the flow behavior in the pulsed column. On the other hand, the DYNAC adopted a back mixing model. However, if reconsideration of the flow model is taken, more exact simulation or simpler calculation may be possible. Particularly, in case of multi-component system, which has not only uranium and plutonium but also other components, a simple flow model is better, because it takes long time for calculation of equiriblium and reaction behavior of the components in the pulsed column.

For the centrifugal contactor, no simulation code has been developed until now. The simulation code for the mixer-settler, however, may be used for the centrifugal contactor,

---

[1] This code is also possible to simulate the mixer-settler extractor.

because its stage regards equilibrium one.

Some informations are required to simulate the extraction process. The distribution coefficients of uranium, plutonium, nitric acid and the other components are essential informations for the extraction process. Many workers have measured the distribution coefficients of these between TBP/n-alkane diluent and nitric acid solution for wide range of solute concentration. Many of these data have been published by Kolarik et al.[12]. The distribution coefficients depend on the solute concentrations in the system, because the solution is non ideal. Two approaches of the distribution coefficients estimation have been developed. One approach is preparation of distribution coefficient database. In this approach, a proper distribution coefficient is retrieved the database and interpolated by the retrieved data. Milles et al. have developed a DISCOSEARCH[13], which is computerized retrieval system for the distribution coefficients, along this approach. The other approach is establishment of some predetermined estimation equations from the distribution data. It is convenient for programing the simulation code because desired distribution coefficient can be calculated explicitly. All the simulation codes stated above have been introduced the estimation equations of the distribution coefficients along this approach. Horner has proposed the estimation equations in the SEPHIS code[6]. His equations are the functions depending on an ionic strength of the aqueous phase. On the other hand, Richardson has proposed the equations that depends on total nitrate ion concentration in the aqueous phase and introduced it into the SEPHIS code[14]. The other codes except the SEPHIS have also used the similar equations by Horner and Richardson.

Reaction kinetics and equilibrium criteria are also required to simulate the extraction process, particularly U-Pu partition process. Reduction kinetics of Pu(IV) to Pu(III) by U^{4+} and hydroxylamine nitrate (HAN) are studied by Newton[15] and Barney[16], respectively. Several reactions concerning the above reactions, such as decomposition of HNO_2 by hydrazine[2][17], have been also studied. If the numerical simulations are carried out in view of the safety and the waste minimization, the reaction kinetics and the equilibrium criteria concerning the other component except uranium and plutonium are required. These kind of researches, however, are not many in the past. Particularly, extraction experiments of the laboratory or plant scale cannot almost be seen in the open literature. In spite of this situation, Tachimori has developed an EXTRA-M simulation code[18] collecting the reaction kinetics data concerning with not only U and Pu but also Np, Tc and Zr, recently. Since the researches like this are just starting, more researches should be required to promote the reliability of such the simulation code.

I-2-3. Process Flowsheet Calculation

Process flowsheet calculation is required to design the Purex process and to decide a proper operational condition. Several flowsheet calculation programs for design and simulation

---

[2] $HNO_2 + N_2H_4 \dashrightarrow HN_3 + 2\ H_2O$

Since nitrous acid produced by these reactions causes reoxidation of Pu(III), hydrazine is required as a stabilizer.

of the general chemical process have been on the market[19]. Some of them could be also used for design and operation of the nuclear fuel reprocessing. REPROCX[20] have been developed at Harwell laboratory as a flowsheet calculation system for the reprocessing process in order to facilitate linking several established simulation codes. It also contains a plenty of knowledge and experiences of UK fuel reprocessing. The REPROCX, however, would be unsuitable to modify the process structure easily. Therefore, though it is convenient for decision of the operational condition to an established plant, it is not suitable for planning and designing the plant based on a new concept. For the researches and developments having the view point of the safety and the waste minimization, a flexible flowsheet calculation system is strongly desired.

I-3. Summary of the Thesis

In this thesis, the followings are carried out;

(i) Reconsideration of the numerical model for the dissolution and the extraction process.

(ii) Extension of the numerical model that can simulate the behavior of not only the uranium and plutonium but also other components in the system.

(iii) Development of the Purex process flowsheet calculation system.

The numerical model always has several model parameters, such as rate and equilibrium constants. A nonlinear least squares method was applied to determine the model parameters through the works. This approach is valid for the hot experiment that is hard to carry out many times.

This thesis consists of seven chapters. The first chapter is introduction of this thesis. Dynamic model for uranium dissolution are introduced in the second chapter[21,22]. The dissolution rate equations are determined from experiments of uranium dioxide pellets dissolution. A new flow model of the pulsed column used at the extraction process is proposed in the third chapter[23]. Dynamic simulation of the pulsed column is also carried out by using of this model[24]. Analysis of neptunium behavior in the extractor is described in the next two chapters. Since the quantity of neptunium in the spent MOX or FBR fuel will increase compared with the conventional LWR fuels in the near future, the neptunium is an important nuclide except uranium and plutonium in the Purex process. The behavior of neptunium in the TBP/n-dodecane-nitric acid system, however, is very complicated. Simulation of its behavior requires both data of extraction equilibria between organic and aqueous solution and of oxidation-reduction reactions in the nitric acid solution. In the 4-th chapter, a new estimation equation of the neptunium distribution coefficient is proposed[25]. The estimation equations for the distribution coefficients of uranium, plutonium and nitric acid are also remade in this chapter. The oxidation-reduction reactions in the nitric acid solution are briefly summarized in the last section in this chapter. An analysis of an oxidation-reduction reaction between Np(V) and Np(VI) with nitrous acid is described in the 5-th chapter[26]. For the analysis, a new approach building the simulation code is also suggested to easily extend the multi-component extraction system. In this chapter, the rate equation of the reaction is developed from the experimental extraction data by the simulation code based on the new approach. In the 6-th chapter, an introduction of the Purex process flowsheet design and analysis system is stated[27]. A feasible study of neptunium separation in the Purex process is also carried out in this chapter. Finally, the conclusion of this thesis is described in the 7-th chapter.

References

1) Benedict, M., Pigford, T.H., Levi, H.W.: "Nuclear Chemical Engineering", (1981), McGraw-Hill.

2) Taylor, R.F., Sharratt, E.W., Chazal, L.E.M., Logsdail, D.H.: "Dissolution Rates of Uranium Dioxide Sintered Pellets in Nitric Acid", *J.Appl.Chem.*, **13**, 32 (1963).

3) Shabbir, M., Robins, R.G.: "Kinetics of the Dissolution of Uranium Dioxide in Nitric Acid I", *ibid.*, **18**, 129 (1968).

4) Shabbir, M., Robins, R.G.: "Kinetics of the Dissolution of Uranium Dioxide in Nitric Acid II", *ibid.*, **19**, 52 (1969).

5) Hodgson, T.D.: "A Model for Fuel Dissolution via Fragmentation", *RECOD*'87, vol.2, 591 (1987).

6) Horner, D.E.: "A Mathematical Model and A Computer Program for Estimating Distribution Coefficients for Plutonium, Uranium and Nitric Acid with Tri-n-butylphosphate", *ORNL-TM*-2711, (1970).

7) Gonda, K., Oka, K., Fukuda, S.: "Calculation Code Revised MIXSET for Purex Process", *PNCT*-841-79-26(in Japanese), (1979).

8) Gonda, K., Matsuda, T.: "Solvent Extraction Calculation Model for Purex Process in Pulsed Sieve Plate Column", *J.Nucl.Sci.Technol.*, **23**[10], 883 (1986).

9) Nabeshima, M., Kitahara, M., Tanaka, C., Shuto, M.: "Dynamics Simulation Code "DYNAC" for the Purex Extraction Cycle Composed of Pulse Columns", *I.Chem.E.Symp.Series* 103, 307 (1987).

10) Petrich, G., Galla, U., Goldacker, H., Schmieder, H.: "Electro Reduction Pulsed Column for the Purex Process, Operational and Theoretical Results", *Chem.Eng.Sci.*, **41**(4), 981 (1986).

11) Levenspiel, O.: "Chemical Reaction Engineering, 2nd Ed.", (1972), John Wiley & Sons.

12) Petrich, G., Kolarik, Z.: "The 1981 Purex Distribution Data Index", *KfK*3080, (1981).

13) Mills, A.L., Ross, R.: "DISCOSEARCH - A Computerized

storage and Retrieval System for Purex Distribution Data", *Proc.ISEC*'86, vol.I, 421 (1986).

14) Richardson, G.L., Swanson, J.L.: "Plutonium Partitioning in the Purex Process with Hydrazine-Stabilized Hydroxylamine Nitrate", *HEDL-TME*7531, (1975).

15) Newton, J.W.: "The Kinetics of the Reaction between Pu(IV) and U(IV)", *J.Phys.Chem.*, **63**, 1493 (1959).

16) Barney, G.S.: "A Kinetic Study of the Reaction of Plutonium(IV) with Hydroxylamine", *J.Inorg.Nucl.Chem.*, **38**, 1677 (1976).

17) Perrott, J.R., Stedman, G., Uysal, N.: "Kinetic and Product Study of the Reaction between Nitrous Acid and Hydrazine", *J.Chem.Soc.*, *Dalton Trans.*, 2058 (1976).

18) Tachimori, S.: "EXTRA·M: A Computer Code System for Analysis of the Purex Process with Mixer Settlers for Reprocessing", *JAERI*-1331(in Japanese), (1994).

19) Biegler, L.T.: "Chemical Process Simulation", *Chem.Eng.Prog.*, **85**[10], 50 (1989).

20) Harrison, J.W., Mills, A.L., Wilkins, M.: "REPROCX - A Reprocessing Flowsheet Computational System", *Proc.ISEC*'86, **1**, 131 (1986).

21) Koga, J., Homma, S., Kanehira, O., Matsumoto S., Goto, M., Yasu, T., Kawata, T.: "Fuel Dissolution Rate and Its Mechanism", *RECOD*'91, vol.II, 687 (1991).

22) Homma, S., Koga, J., Matsumoto, S., Kawata, T.: "Dissolution Rate Equation of UO_2 Pellet", *J.Nucl.Sci.Tecnol.*, **30**[9], 959 (1993).

23) Homma, S., Koga, J., Matsumoto, S.: "Extraction Calculation of Pulsed Column by Progression Model", *ibid.*, **28**[9], 873 (1991).

24) Homma, S., Koga, J., Matsumoto, S., Fujine, S., Maeda, M.: "Extraction Dynamics of Pulsed Column in the Purex Process", *Proc.ISEC*'90, Part A, 615 (1992).

25) Homma, S., Takanashi, M., Koga, J., Matsumoto S.: "Estimation of Distribution Coefficients of U(VI), Pu(IV) and Np(VI) in HNO_3-30%TBP/n-alkane System", *Sci.Eng.Reports Saitama Univ.*, **27**, 5 (1993).

26) Homma, S., Koga, J., Matsumoto S.: "Evaluation of Aqueous Reactions in Purex Extraction Process", *RECOD*'94, vol.III (1994).

27) Homma, S., Sakamoto, S., Takanashi, M., Nammo, A., Satoh, Y., Soejima, T., Koga, J., Matsumoto S.: "Development of COMPAS, Computer Aided Process Flowsheet Design and Analysis System of Nuclear Fuel Reprocessing", *J.Nucl.Sci.Tecnol.* (in press).

CHAPTER II

DISSOLUTION EQUATION OF UO_2 PELLET

II-1. Introduction

The dissolution of spent nuclear fuel is head-end process of the Purex process. The dissolution behavior influences the next extraction cycle and off-gas treatment process. The rate and the mechanism of the dissolution of the fuel ,therefore, are the important factors for design and operation of the fuel reprocessing. Several authors have investigated the kinetics of dissolution of uranium dioxide in nitric acid solution experimentally[1~4]. Since the fuel dissolution proceeds by both of penetration of solution into a pellet and several chemical reactions, the rate equation, however, is complicated. Taylor et al. have attempted to make a qualitative assessment of whether the process is controlled by chemical kinetics or by diffusion of reacting species and the initial rate of dissolution has been attributed to the build-up of nitrite ions which then catalyze further dissolution[1]. Shabbir et al. have attempted to allow for a changing surface area for dissolution by assuming that the dissolution occurs uniformly at the external surfaces of fuel pellets[2,3]. This approach is only applicable to describe the initial dissolution rate.

Hodgson[5] have proposed a dissolution model which is expressed by two step scheme as:

$$W_{ue} \dashrightarrow W_e \dashrightarrow W_d \qquad \text{(II-1)}$$

where W_{ue} is unexposed mass of fuel, W_e is exposed mass and W_d is dissolved one. The former process in Eq.(II-1) is considered as the penetration process and the penetration rate may be proportional to nitric acid concentration in the solution. While, the later is considered as the chemical reaction one. His model, however, was based on physical aspect, so that no explanation for chemical reaction kinetics was given. In this study, the model is extended to represent the dissolution process which is controlled by both the penetration and the reaction. The present model is based on experimental observations with the unirradiated oxide fuel.

II-2. Experimental

A schematic diagram of experimental apparatus is shown in **Fig.II-1**. The solution in the dissolver was heated by a hot plate and was kept at constant temperature. The solution was also agitated with a magnetic stirrer while dissolution. Nitrogen gas was fed into the dissolver in order to sweep NO gas which was generated by the dissolution reactions. Some cylindrical unirradiated UO_2 pellets (ϕ14.5×20.0 mm) were dissolved in the nitric acid solution of 500 ml at the temperature of 353 K (80 °C), 368 K (95 °C) and 378 K (105 °C). The initial normality of nitric acid were 5, 6 and 7 N and the initial uranyl concentration was changed from zero to 160 g/l in each normality of the acid. The solution of 1.5 ml was collected every 15 minutes in order to measure the uranyl ion and the acid concentration. The uranyl ion and the acid concentration were measured by absorptiometry at 415 nm and the potentiometric titration used with NaOH, respectively.

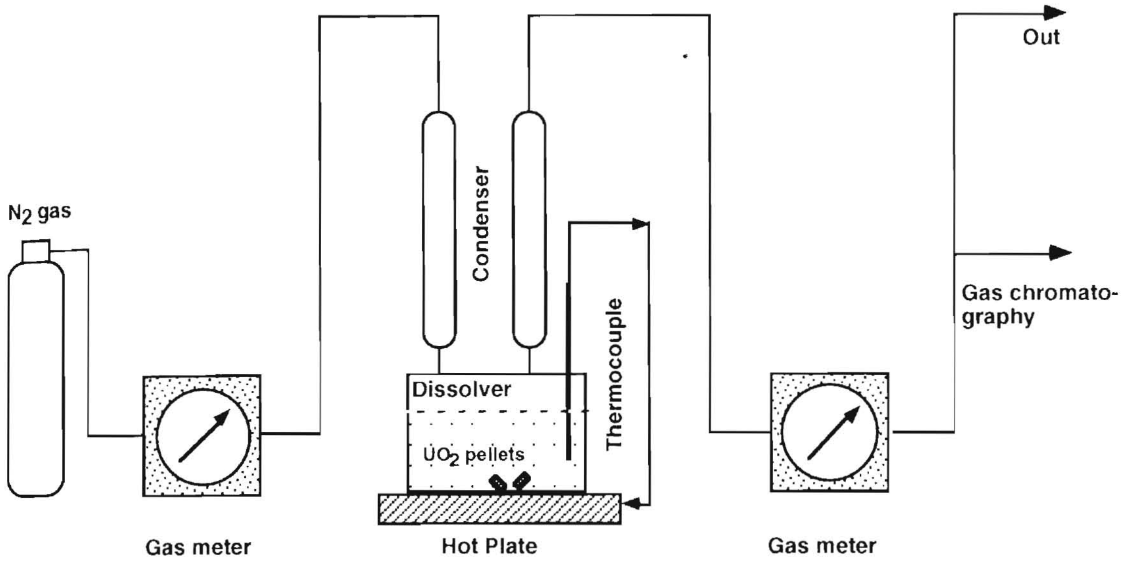

Fig.II-1 Schematic diagram of experimental apparatus

II-3. Results and Discussion

The reactions between UO_2 and ions in the nitric acid solution under these experimental conditions are assumed as follows[1,2]:

$$3\ H^+ + NO_3^- + UO_2 \xrightarrow{k_n} UO_2^{2+} + HNO_2(aq) + H_2O \qquad (II\text{-}2)$$

$$2\ HNO_2(aq) + 2\ H^+ + UO_2 \xrightarrow{k_n} UO_2^{2+} + 2\ NO(gas) + 2\ H_2O. \qquad (II\text{-}3)$$

The experimental results show that the dissolution rate of UO_2 is promoted with increase of the initial concentration of uranyl ions as shown in **Fig.II-2**. Therefore, the catalyzed reaction by the uranyl ions is also assumed as:

$$H^+ + NO_3^- + UO_2^{2+} + UO_2 \xrightarrow{k_c} 2\ UO_2^{2+} + HNO_2(aq) + H_2O. \qquad (II\text{-}4)$$

Thus, the dissolution rate equations based on both the penetration process and the above reaction schemes are given as:

$$dW_{ue}/dt = -k_p[\mathrm{HNO_3}]W_{ue} \tag{II-5}$$

$$dW_e/dt = k_p[\mathrm{HNO_3}]W_{ue} - (k_h[\mathrm{HNO_3}]^\alpha + k_n[\mathrm{HNO_2}]^\beta[\mathrm{HNO_3}]^\chi + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon)W_e \tag{II-6}$$

$$d[\mathrm{UO_2}^{2+}]/dt = (1/M_{\mathrm{UO2}}V)(k_h[\mathrm{HNO_3}]^\alpha + k_n[\mathrm{HNO_2}]^\beta[\mathrm{HNO_3}]^\chi + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon)W_e \tag{II-7}$$

$$d[\mathrm{HNO_3}]/dt = (8/3)(1/M_{\mathrm{UO2}}V)(k_h[\mathrm{HNO_3}]^\alpha + k_n[\mathrm{HNO_2}]^\beta[\mathrm{HNO_3}]^\chi + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon)W_e \tag{II-8}$$

$$d[\mathrm{HNO_2}]/dt = (1/M_{\mathrm{UO2}}V)(k_h[\mathrm{HNO_3}]^\alpha - 2k_n[\mathrm{HNO_2}]^\beta[\mathrm{HNO_3}]^\chi + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon)W_e \tag{II-9}$$

where k_p is a rate constant of penetration process in Eq.(II-1), M_{UO2} is molecular weight of $\mathrm{UO_2}$ and V is volume of reacting solution. Now, the steady-state approximation can be applied to the nitrous acid concentration as:

$$k_h[\mathrm{HNO_3}]^\alpha - 2k_n[\mathrm{HNO_2}]^\beta[\mathrm{HNO_3}]^\chi + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon = 0. \tag{II-10}$$

Equations (II-6), (II-7) and (II-8) are rewritten by using Eq.(II-10) as:

$$dW_e/dt = k_p[\mathrm{HNO_3}]W_{ue} - (3/2)(k_h[\mathrm{HNO_3}]^\alpha + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon)W_e \tag{II-11}$$

$$d[\mathrm{UO_2}^{2+}]/dt = (3/2)(1/M_{\mathrm{UO2}}V)(k_h[\mathrm{HNO_3}]^\alpha + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon)W_e \tag{II-12}$$

$$d[\mathrm{HNO_3}]/dt = (8/3)(2/M_{\mathrm{UO2}}V)(k_h[\mathrm{HNO_3}]^\alpha + k_c[\mathrm{HNO_3}]^\delta[\mathrm{UO_2}^{2+}]^\varepsilon)W_e. \tag{II-13}$$

Consequently, nitrous acid concentration, rate constant k_n in Eq.(II-3) and reaction orders β and χ are eliminated in the rate equations above. Time changes of W_{ue}, W_e, $[\mathrm{UO_2}^{2+}]$ and

$[HNO_3]$ were calculated by solving the simultaneous differential equations of Eqs.(II-5), (II-11), (II-12) and (II-13) numerically. The rate constants k_p, k_h and k_c and the reaction orders α, δ and ε were determined to minimize the difference between the calculated uranyl ion concentration and experimental one by the quasi-Newton method which is one of the non-linear optimization technique[6].

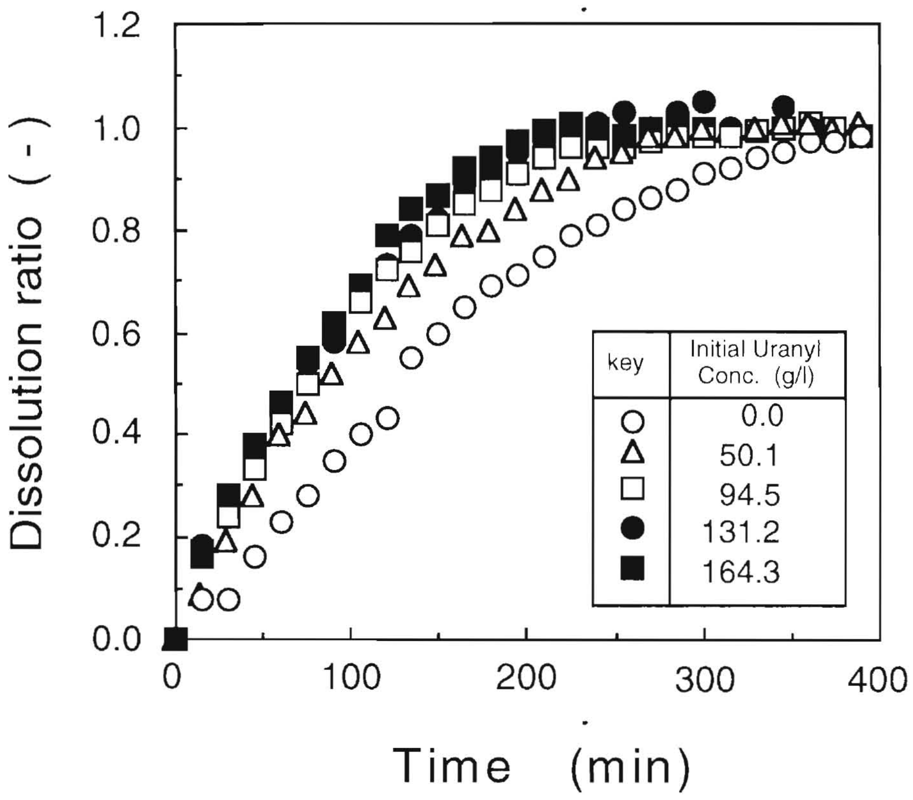

Fig.II-2 Effect of initial uranyl ion concentration, $[UO_2^{2+}]_{init}$, on time changes of dissolution ratio in 5 N HNO_3 at 368 K

Table II-1 shows the penetration and reaction rate constants and the reaction orders determined by the above method. The reaction rate constant of catalyzed reaction by uranyl ion k_c was almost constant for each experimental condition. **Figure**

II-3 shows the dissolution curve of 31.5 g UO_2 pellet at 368 K. The initial concentration of nitric acid and uranyl ion were 5.0 N and 94.5 g/l, respectively. The dissolution curve calculated by the presented rate equations is in good agreement with the experimental one. On the other hand, 4 pellets (140.5 g) were dissolved in 7.0 N nitric acid solution at 378 K as shown in **Fig.II-4**. The calculated dissolution curve is also in good agreement with the experimental one. It is concluded that the rate equations derived in this study are applicable for wide range of uranyl ion concentration.

Table II-1 Penetration and reaction rate constants and reaction orders

k_p	[(l/mol)/min]	$2.10\times10^{-3}\pm4.3\times10^{-4}$
k_h	[(l/mol)^2/min]	$2.91\times10^{-3}\pm4.7\times10^{-4}$
k_c	[(l/mol)^3/min]	5.00×10^{-4}
α		2.0
δ		2.0
ε		1.0

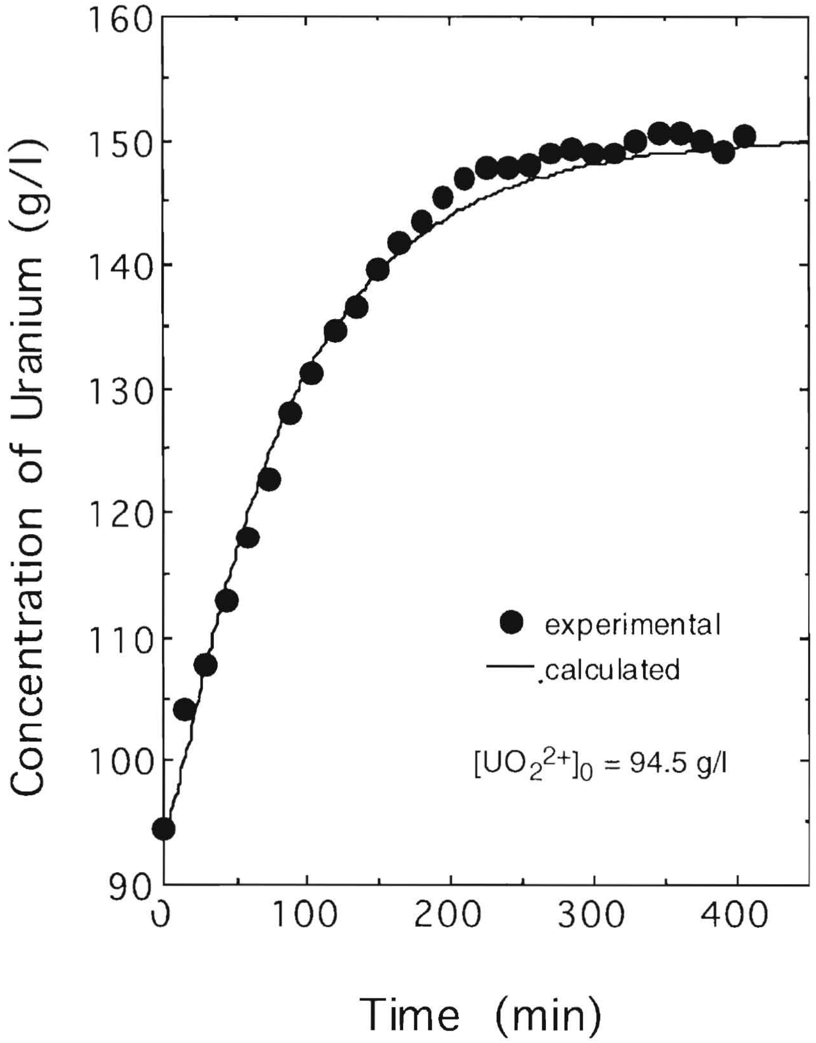

Fig.II-3 Dissolution curve of one pellet (31.5 g) in 5 N HNO_3 at 368 K

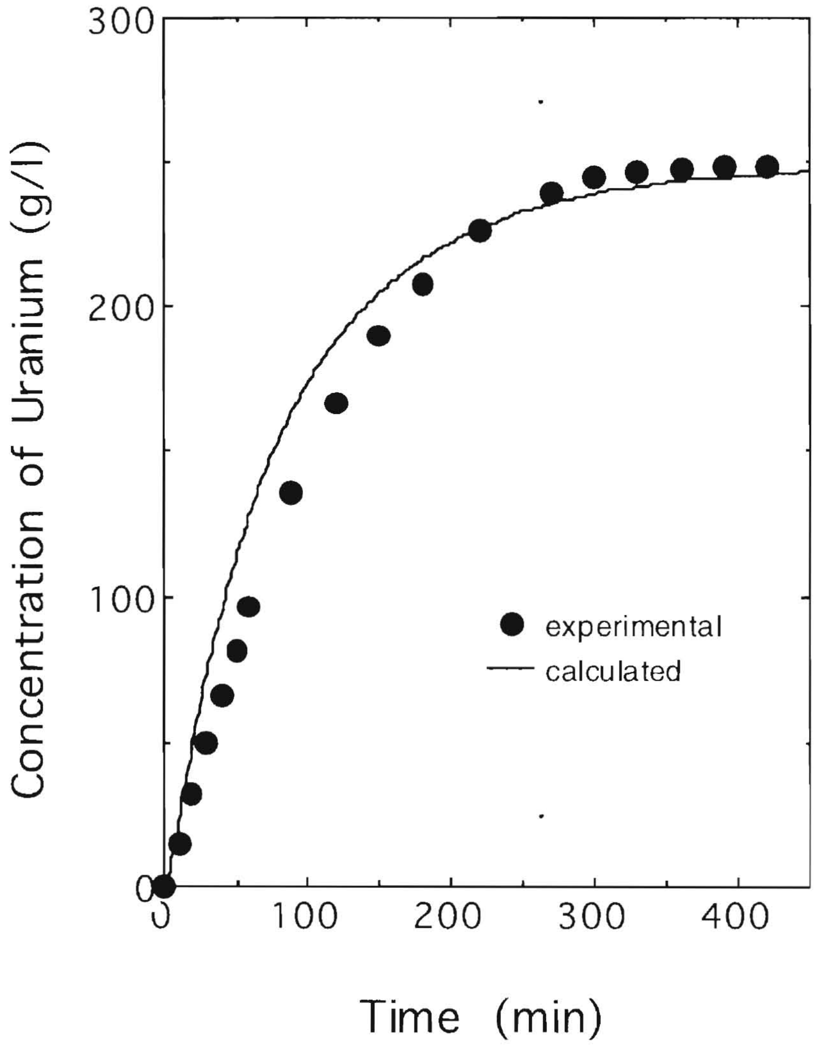

Fig.II-4 Dissolution curve of four pellets (140.5 g) in 7 N HNO_3 at 378 K

II-4. Conclusion

The dissolution model reported by Hodgson was extended to describe the dissolution rate depending upon the solute concentration in the dissolution. The model also described the dissolution process, which are controlled by both penetration and reaction. The reaction orders and the rate constants in the model were determined by the nonlinear least squares method. The presented model is based upon the experimental observations with the unirradiated oxide fuel, nevertheless it should be easily extended to the irradiated oxide fuels. The rate equations presented here should be applicable to simulation for a batch dissolver or a continuous one.

References

1) Taylor, R.F., Sharratt, E.W., Chazal, L.E.M., Logsdail, D.H.: "Dissolution Rates of Uranium Dioxide Sintered Pellets in Nitric Acid", *J.Appl.Chem.*, **13**, 32 (1963).

2) Shabbir, M., Robins, R.G.: "Kinetics of the Dissolution of Uranium Dioxide in Nitric Acid I", *ibid.*, **18**, 129 (1968).

3) Shabbir, M., Robins, R.G.: "Kinetics of the Dissolution of Uranium Dioxide in Nitric Acid II", *ibid.*, **19**, 52 (1969).

4) Fukasawa, T., Ozawa, Y., Kawamura, F.: "Generation and Decomposition Behavior of Nitrous Acid During Dissolution of UO_2 Pellets by Nitric Acid", *Nucl.Tecnol.*, **94**, 108 (1991).

5) Hodgson, T.D.: "A Model for Fuel Dissolution via Fragmentation", *RECOD*'87, vol.2, 591 (1987).

6) Press, W.H., Flannery, B.P., Teukolsky, S.A., Vetterling, W.T.:"Numerical Recipes", pp.307~312 (1986), Cambridge Univ.Press, New York.

CHAPTER III

SIMULATION OF PULSED COLUMN BY PROGRESSION MODEL

III-1. Introduction

Several simulation codes of the pulsed column used in the Purex process have been developed for optimum design and operation of it. It is well known that a back mixing exists along the column because of its pulsation[1]. A proper flow model[2], therefore, is required to simulate the extraction behavior in the pulsed column. The flow behavior in the pulsed column has been described by a dispersion model[3] or a back-mixing model[4,5]. **Table III-1** shows the characteristics of the flow models. The back mixing in the column is described by an axial dispersion coefficient and a back-mixing one in the dispersion and the back-mixing models, respectively. On the other hand, a tanks in series model uses the series of mixed tanks to describe the flow behavior. Generally, a degree of the back mixing varies with the axial direction of the column because of its end effect, density change with concentration and so on. These models shown in the table, however, cannot describe the axial change of the back mixing in the column. If the dispersion and the back-mixing models are used to describe the axial change of the back mixing, the axial dispersion and the back-mixing coefficients are the function of the axial coordinate apparently. In the use of the simulation codes applied the back-mixing or dispersion model, therefore, a lot of iteration calculations might be required to determine the concentration profiles of the components in the column.

In this study, the progression model is proposed to simulate the extraction behaviors in the column. In the progression model, the column is virtually divided into the mixed tanks as well as the tanks in series model. Since the each tank has same volume, the tanks in series model has one parameter that is the number of tanks. The progression model has another parameter, the volume of each tank. The volume of each tank in the progression model is different in order to express fairly well the degree of the back mixing along the column.

In the second and third sections in this chapter, verification of the progression model is illustrated. In the 4-th section, simulation of extraction dynamics in the pulsed column is carried out by using of the progression model. It is also shown here that the model is applicable to not only the steady state simulation but also the dynamics.

Table III-1 Flow models used for simulation of the pulsed column

Model:	Dispersion model	Back-mixing model	Tanks in series model
Flow	Plug flow	Mixed flow with back flow	Mixed flow
Parameter:	Axial dispersion coefficient	Back-mixing coefficient	Number of mixed tank
Code:	PULCO[3], VISCO[6]	DYNAC[5]	(SEPHIS[7], MIXSET[8])*

* Although they have been developed for the mixer-settler, they can be used for the simulation of the pulsed column.

III-2. Progression Model and Calculation Procedure

Figure III-1 shows the material balance of the progression model, schematically. When the mass transfer occurs from aqueous to organic phase, the material balance equations of the progression model without chemical reaction terms are given as:

$$\phi_x v_i \frac{dx_{i,j}}{dt} = Q_x x_{i-1,j} - Q_x x_{i,j} - K_d a v_i \left(y^*_{i,j} - y_{i,j} \right) \qquad \text{(III-1)}$$

$$\phi_y v_i \frac{dy_{i,j}}{dt} = Q_y y_{i+1,j} - Q_y y_{i,j} + K_d a v_i \left(y^*_{i,j} - y_{i,j} \right) \qquad \text{(III-2)}$$

$$y^*_{i,j} = D_{i,j} x_{i,j} \qquad \text{(III-3)}$$

where, ϕ is the fractional holdup, Q is the volumetric flow rate, and x and y are the solute concentration in aqueous and organic phase respectively. The overall mass transfer coefficients based on dispersed phase $K_d a$, are obtained by using the two-film theory[9]. Organic phase holdup ϕ_y is assumed to be uniform along the column. Distribution coefficients $D_{i,j}$ are given as functions of nitrate ion and uncomplexed (free) TBP concentrations[10].

Equations (III-1) and (III-2) are integrated numerically from an arbitrary initial condition until steady state is achieved. These equations were rewritten in the finite difference form by the complete implicit method.

The volume of each tank V_i and the number of tanks were determined by minimizing the difference between the experimental steady-state concentration profiles of uranium, plutonium and nitric acid in organic phase and calculated ones. The problem of finding the best values of the volume and the number of tanks was solved by the Complex (Constrained simplex) method, which was one of the non-linear optimization technique[11].

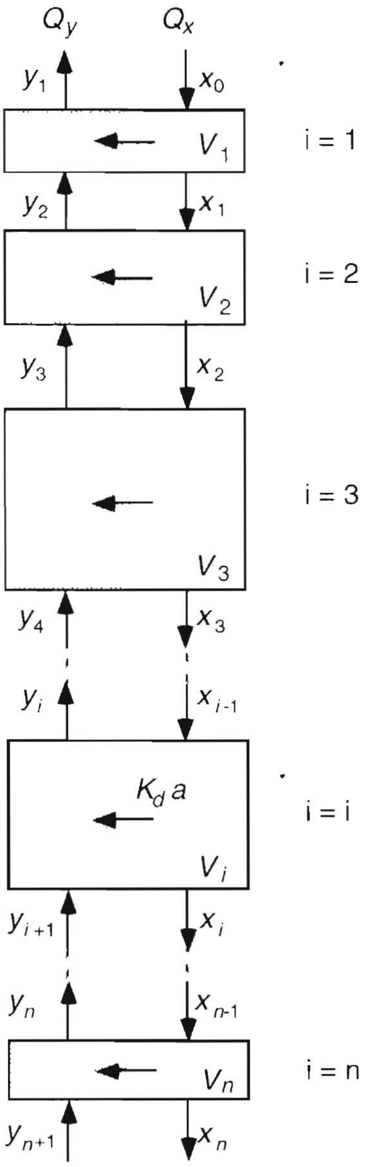

Fig.III-1 Material balance of progression model

III-3. Verification of the Progression Model

Simulations of steady state extraction behavior in the pulsed column are carried out to verify the progression model. **Table III-2** shows the column geometry and the operational conditions in the experiment reported by Gonda et al.[12]. Feed conditions of aqueous and organic phase in the calculation are shown in **Table III-3**.

Table III-2 Column geometry and operational conditions

Column:	Inside diameter	5.0	(cm)
	Column length	200.0	(cm)
Plate:	Type	Sieve	
	Number of plates	36	(-)
	Plate spacing	5.0	(cm)
	Hole diameter	0.3	(cm)
	Free area	23.0	(%)
	Thickness	0.2	(cm)
Pulse conditions:			
	Frequency	40.0	(1/min)
	Amplitude	1.8	(cm)

Figure III-2 shows the comparison between calculated and experimental concentration profiles of uranium and nitric acid in organic phase at the steady state. The calculated concentration profiles of uranium and nitric acid are fairly well agreement with the experimental ones. The number of tanks determined from the profiles was 10. **Figure III-3** shows the tank volume determined by the experimental profiles. The figure implies that the back mixing in the column is not uniform along the axial direction of the column, because the volume of tank is different from each other. **Figure III-4** also shows the calculated and experimental concentration profiles of uranium, plutonium and nitric acid in organic phase. The optimized tank volume is also shown in **Fig.III-5**. The calculated concentration profiles of uranium, plutonium and nitric acid are also in good agreement with the experimental ones. It is concluded that the progression model is applicable to the steady state simulation of the pulsed column

Table III-3 Feed conditions of aqueous and organic phase for Figs.III-2 and III-4

	Aqueous phase (dispersed phase)		Organic phase (continuous phase)	
	Fig.III-2	Fig.III-4	Fig.III-2	Fig.III-4
Flow rate (cm^3/s)	1.89	2.08	3.67	3.67
Concentration:				
U(VI) (g/l)	200.0	97.0	0.0	0.0
Pu(IV) (g/l)	0.0	8.3	0.0	0.0
HNO_3 (mol/l)	3.12	3.2	0.0	0.0
TBP (%)	-	-	30.0	30.0

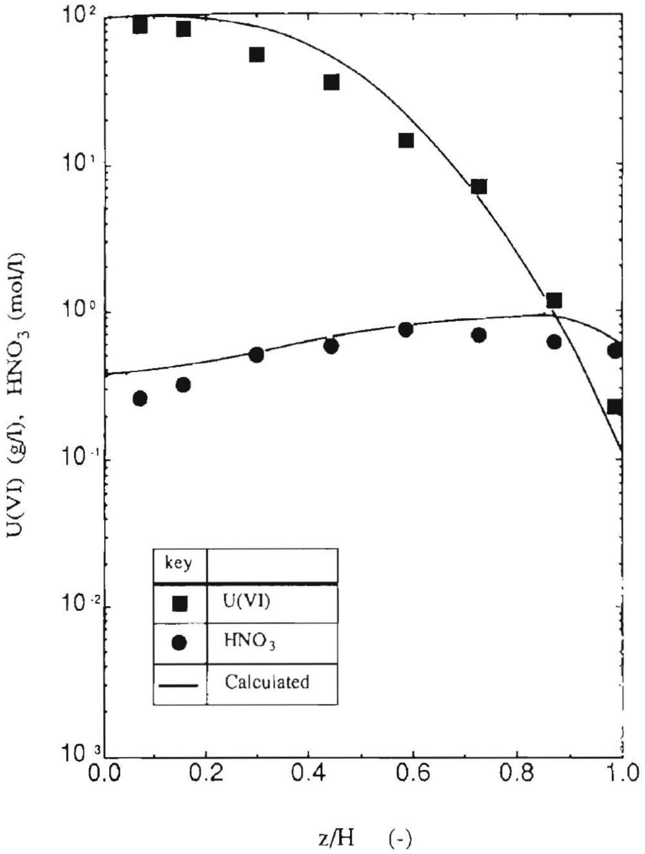

Fig.III-2

Comparison between calculated and experimental concentration profiles of uranium and nitric acid in organic phase

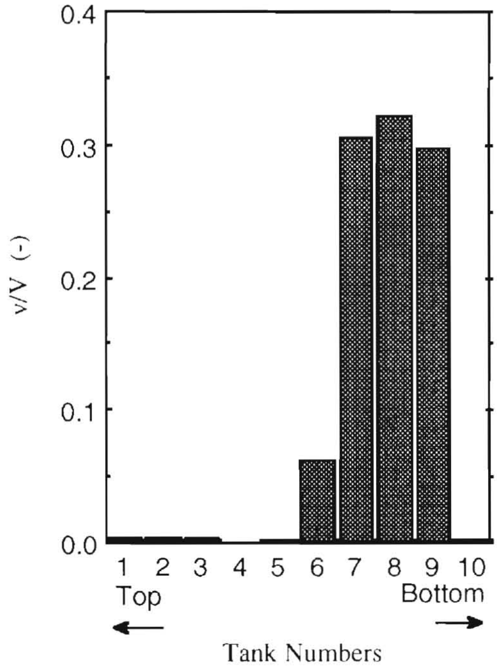

Fig.III-3

Axial change of tank volume in calculation of Fig.III-2

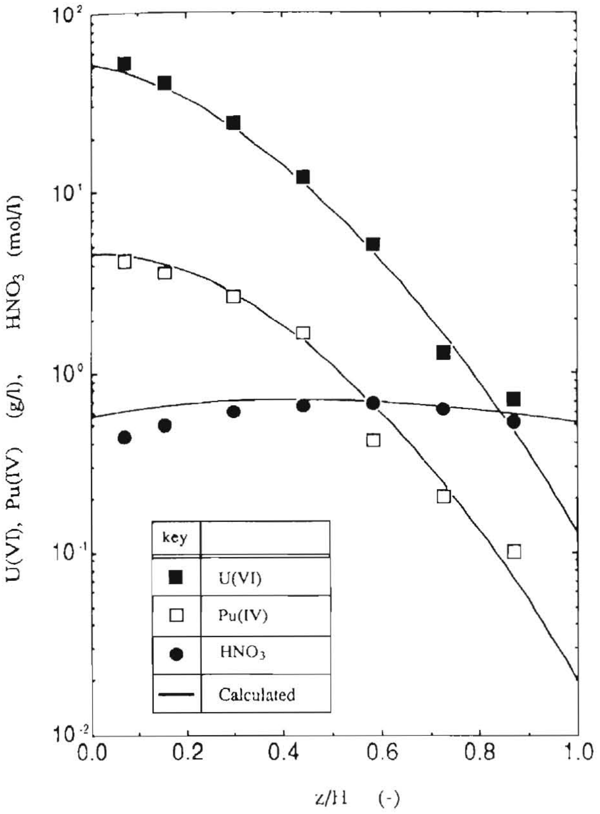

Fig.III-4

Comparison between calculated and experimental concentration profiles of uranium, plutonium and nitric acid in organic phase

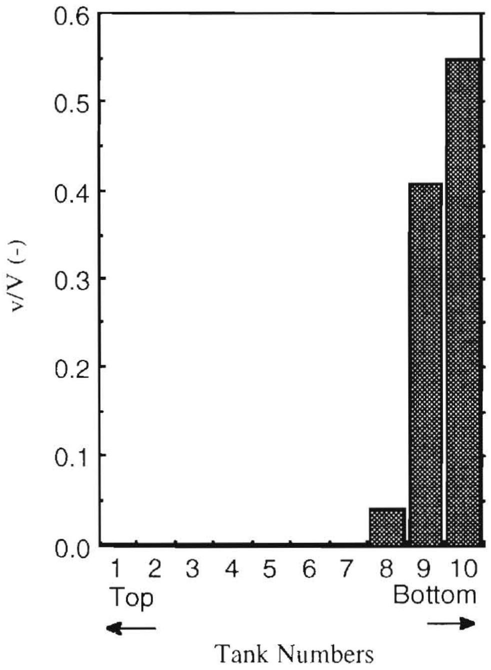

Fig.III-5

Axial change of tank volume in calculation of Fig.III-4

III-4. Dynamic Simulation of Pulsed Column by Progression Model

In this section, applicability of the progression model to the simulation of extraction dynamics of the pulsed column is discussed. Experimental transient response curves of uranyl nitrate were obtained by a 4 m-long annular pulsed column with baffle plates.

III-4-1. Experimental

A schematic diagram of the experimental apparatus is shown in **Fig.III-6**. The annular pulsed column with two-hundreds of baffle plates was used for uranium extraction. The effective height of the column made from stainless steel was 4 m-long. The inner tube of the annular was 89 mm in outside diameter and the outer one was 165 mm in inside diameter. The baffle plates with 23 % free area were also made from stainless steel and the plate spacing was 2 cm. Three sampling ports for measuring the organic phase concentration and the organic phase holdup were set at 1 m intervals from top of the column. A sampling port for solvent extract was also set at its drain tube. Operational conditions are shown in **Table III-4**.

The experimental transient response curves were obtained by introducing a step change in the aqueous feed solute concentration at the top of the column. Before the step change was carried out, the column was operated with solute free streams in order to reach the hydraulic stability. The extract and the organic phase in the column were sampled every 2 minutes. The concentration of uranyl ion and nitric acid were measured by potentiometric titration.

Table III-4 Operational conditions

Aqueous phase flow rate, Q_x		20.50	[cm^3/s]
Organic phase flow rate, Q_y		40.83	[cm^3/s]
Aqueous feed concentration:			
	U(VI)	158.5	[g/l]
	HNO_3	3.12	[mol/l]
Pulse conditions:			
	Frequency	55.0	[cpm]
	Amplitude	2.00	[cm]
Dispersed phase:		Aqueous	

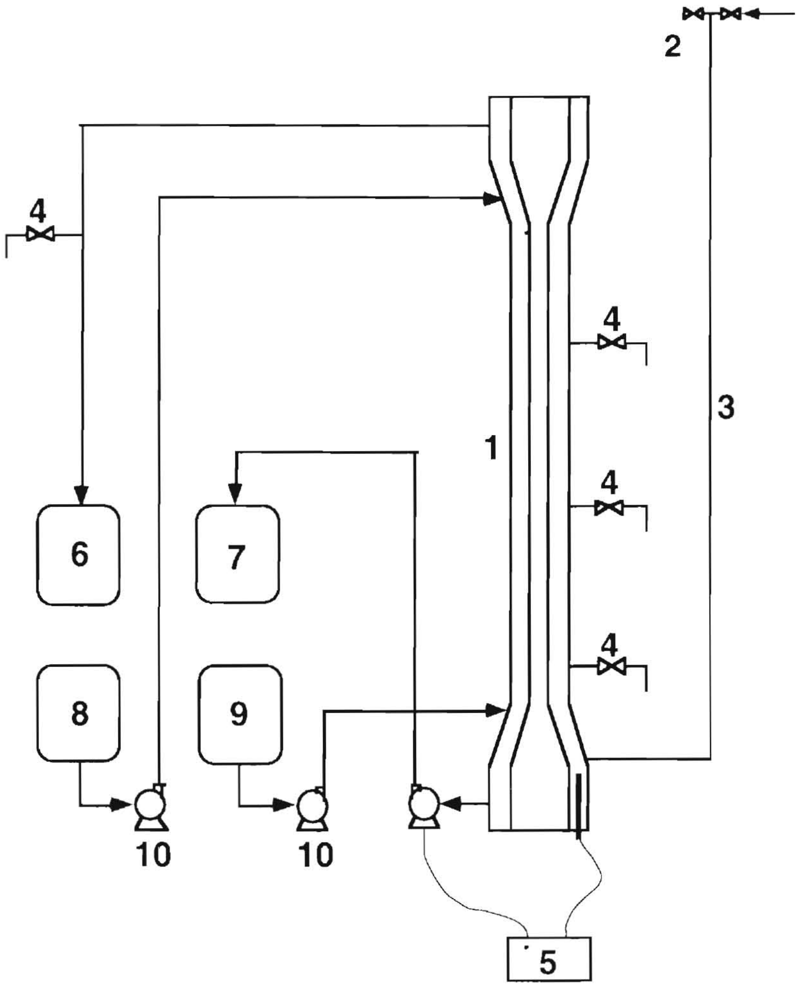

Fig.III-6 Schematic diagram of the experimental apparatus (1:Annular pulsed column with baffle plates, 2:Pulse generator, 3:Pulse leg, 4:Sampling ports, 5:Interface controller, 6:Solvent extract storage vessel, 7:Raffinate storage vessel, 8:Aqueous feed storage vessel, 9:Organic feed storage vessel, 10:feed pumps)

III-4-2. Results and Discussion

Figure III-7 shows the steady state concentration profiles of uranium and nitric acid in organic phase. Dispersed phase (aqueous phase) holdup was about 5 % through the operation. The number of tanks determined by using this profiles were 9 and the change of tank volume was determined as shown in **Fig.III-8**.

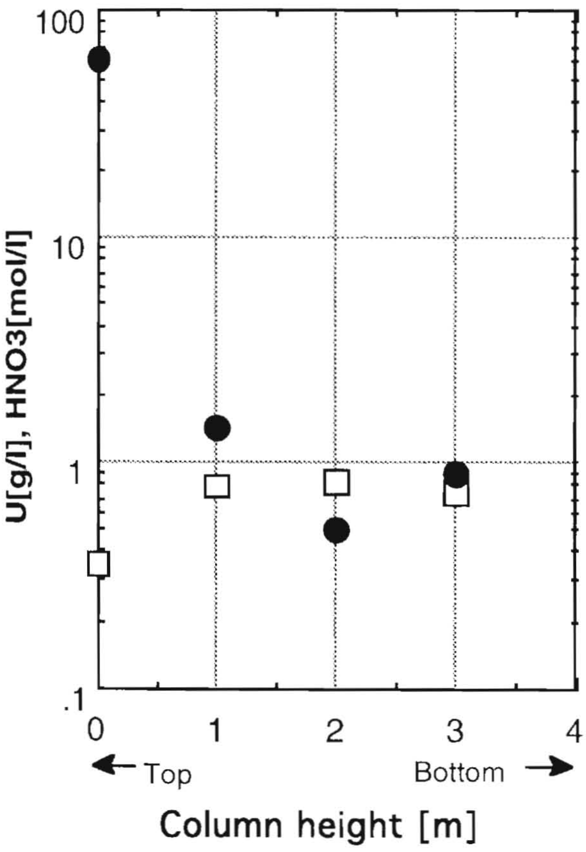

Fig.III-7 Organic phase steady state concentration profiles
□:nitric acid,
●:uranyl nitrate

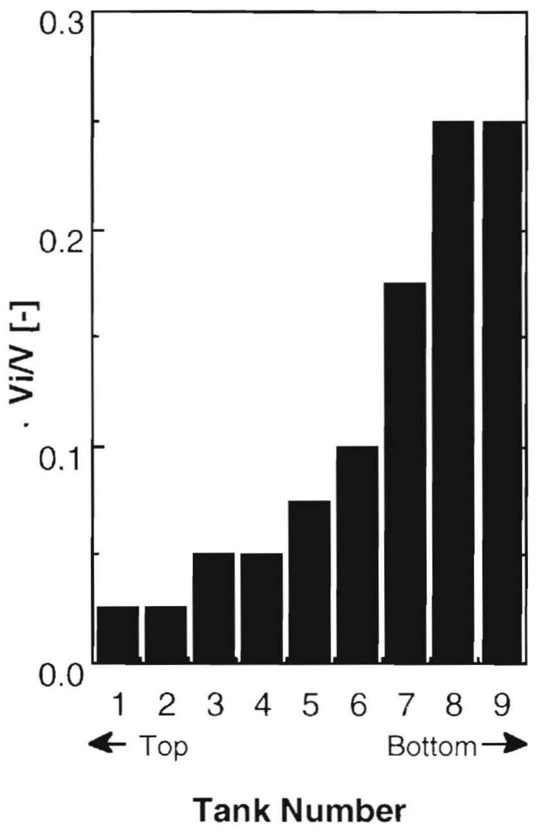

Fig.III-8 The volume of each tank determined by using Fig.III-7

The simulation of dynamic behavior of uranium was carried out by solving Eqs.(III-1), (III-2) and (III-3) using the number of tanks and the volume of each one determined. **Figures III-9 (a)** and **(b)** show the time change of uranium concentration in the extract and the organic phase at the sampling port under 1 m from the top of the column, respectively. The time to reach steady state was about 50 minutes in the experiment. Since the calculated results using the number of tanks and the volume of each one show good agreement with the experimental ones, this model is adequate to the simulation of extraction dynamics in the pulsed column.

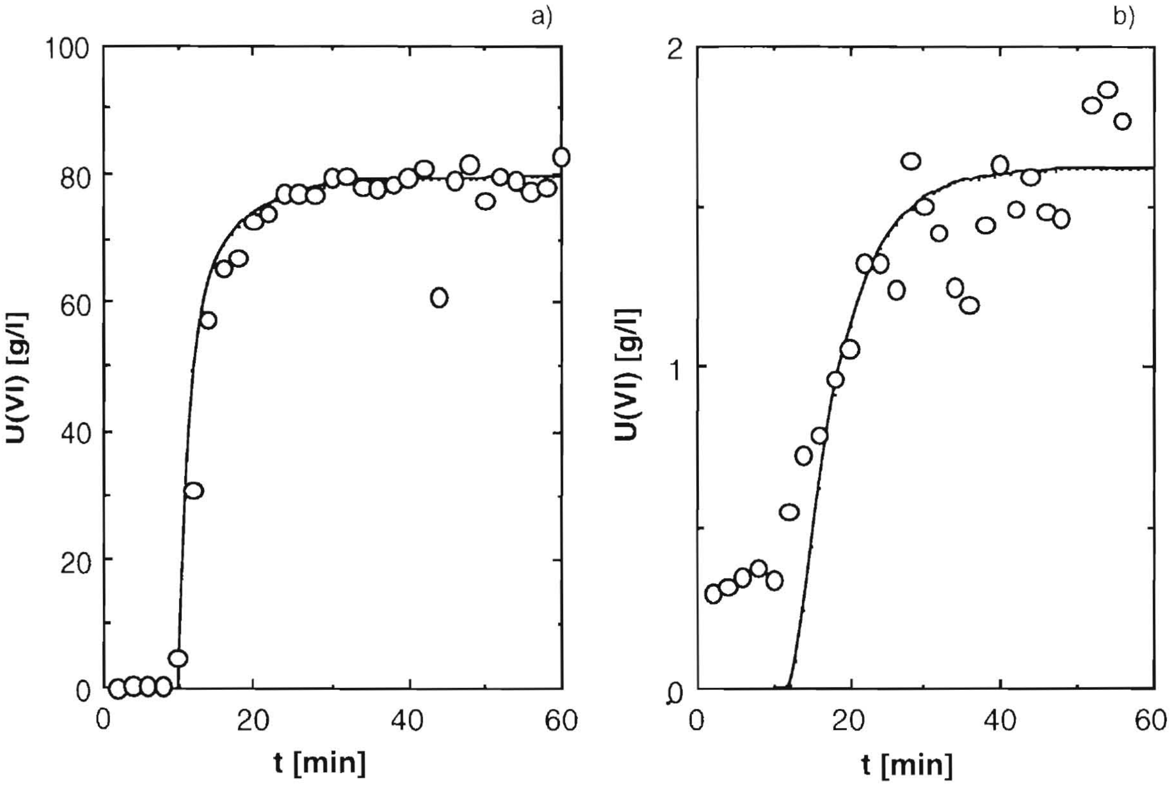

Fig.III-9 Comparison of simulated transient response curves with experimental data (○:experimental, —:calculated)
(a) extract at the top of the column
(b) organic phase at the sampling port under 1 m from the top of the column

III-5. Conclusion

It is concluded that the progression model is applicable to simulate the steady state extraction behavior in the pulsed column. This model is also applicable to simulate the dynamic behavior of the concentration of uranium in the pulsed column, when the small change of the flow rate of extraction and/or raffinate from the stationary condition. If the the number of tanks and the volume of each one of the progression model are represented as the operational conditions, the model will be more available.

References

1) Matsumoto, S., Homma, S., Koga, J., Kobayashi, H.: "Axial Dispersion Coefficient and Mass Transfer Rate in Pulsed Column", *J.Nucl.Sci.Technol.*, **26**[4], 473 (1989).

2) Levenspiel, O.: "Chemical Reaction Engineering, 2nd Ed.", (1972), John Wiley & Sons.

3) Gonda, K., Matsuda, T.: "Calculation Code PULCO for Purex Process in Pulsed Column", *PNCT*-841-82-19(in Japanese) (1982).

4) Hass, R.T.: "Development and Verification of a Mathematical Model for a Pulsed Extraction Column", *IS-T*-1101, (1984).

5) Nabeshima, M., Kitahara, M., Tanaka, C., Shuto, M.: "Dynamics Simulation Code "DYNAC" for the Purex Extraction Cycle Composed of Pulse Columns", *I.Chem.E.Symp.Series* 103, 307 (1987).

6) Petrich, G., et al.: "Electro Reduction Pulsed Column for the Purex Process, Operational and Theoretical Results", *Chem.Eng.Sci.*, **41**(4), 981 (1986).

7) Horner, D.E.: "A Mathematical Model and A Computer Program for Estimating Distribution Coefficients for Plutonium, Uranium and Nitric Acid with Tri-n-butylphosphate", *ORNL-TM*-2711, (1970).

8) Gonda, K., Oka, K., Fukuda, S.: "Calculation Code Revised MIXSET for Purex Process", *PNCT*-841-79-26(in Japanese), (1979).

9) Tung, L.S., Luecke, R.H.: "Mass Transfer and Drop Sizes in Pulsed-Plate Extraction Columns", *I&EC Process Des.Dev.*, **25**, 664 (1988).

10) Richardson, G.L., Swanson, J.L.: "Plutonium Partitioning in the Purex Process with Hydrazine-Stabilized Hydroxylamine Nitrate", *HEDL-TME*-7531, (1975).

11) Umeda, T., Ichikawa, A.: "A Modified Complex Method for Optimization", *I&EC Process Des.Dev.*, **10**, 229 (1971).

12) Gonda, K., Matsuda, T.: "Solvent Extraction Calculation Model for Purex Process in Pulsed Sieve Plate Column", *J.Nucl.Sci.Technol.*, **23**[10], 883 (1986).

CHAPTER IV

DISTRIBUTION COEFFICIENTS OF NEPTUNIUM AND OXIDATION-REDUCTION REACTIONS OF NEPTUNIUM

IV-1. Introduction

A lot of components must be handled by the numerical simulation in view of the safety and the waste minimization. The simulation codes of the extraction process developed in the past, however, handled almost uranium and plutonium. The code, therefore, should be extend to deal with the other components. In the present situation, the informations of the other components, such as the distribution coefficients and the reaction kinetics, are less than those of uranium and plutonium. In the following two chapters, extension of the simulation model for the other components is discussed. Neptunium is taken up as the typical components except uranium and plutonium for the extension.

The quantity of neptunium in the spent MOX or FBR fuels will increase compared with the conventional LWR fuels in the near future. Neptunium, therefore, will be an important nuclide in the Purex process. The behavior of neptunium in the TBP/n-dodecane-nitric acid system, however, is very complicated. The reasons why are; (i) Neptunium has three valences of IV, V and VI in nitric acid solution under normal Purex extraction condition, (ii) Np(IV) and Np(VI) are extracted by TBP, but Np(V) is not extracted, and (iii) its valence is affected by oxidation-reduction reactions with other components in the system. Simulation of its behavior, therefore, requires both data of extraction equilibria between organic and aqueous solution and of oxidation-reduction reactions in the nitric acid solution.

In this chapter, a new estimation equation of the neptunium distribution coefficient is proposed. The estimation equations of the distribution coefficients for uranium, plutonium and nitric acid are also remade in this chapter. The oxidation-reduction reactions for neptunium in the nitric acid solution are briefly summarized in the last section in this chapter.

IV-2. Estimation Equations of Distribution Coefficients

Distribution equilibrium of nitric acid and actinide, such as uranium, plutonium and neptunium, between aqueous solution and TBP (tri-butyl phosphate) are very interested in Purex extraction process. The estimation equations of the distribution coefficients are required to calculate the concentration profiles of extraction components in the extractor. Many researchers[1~11] have investigated the equilibrium of the nitric acid and uranyl nitrate between aqueous and organic solvents experimentally and theoretically. The results of these studies can be summarized briefly as the followings: (i) Nitric acid is almost extracted by forming 1:1-complex with TBP; (ii) U(VI) are extracted by forming 1:2-complex with TBP such as $UO_2(NO_3)_2(TBP)_2$; (iii) Equilibrium constants of extraction reactions are not conformed with mass action law because of deviation from ideal solutions. Accordingly, the equilibrium constants may be expressed as a function of concentration of solutions. Richardson[12] has suggested that the equilibrium constants were expressed as the functions of total nitrate ion concentration. In this study, the equilibrium constants of extraction reactions between aqueous and organic solvents were correlated to a total ionic strength by a least squares method.

The extraction equilibria of Np(VI), U(VI), Pu(IV) and nitric acid are illustrated and a regression method are briefly stated in the first part of this section. The results of the regression are discussed in the second part of the section. A comparison between the estimation equation presented by the former researchers and the established ones by this study is also carried out here. Determination of the parameters of estimation equations is carried out by using of distribution data reported by Petrich[13].

IV-2-1. Extraction Equilibria and Regression Method

The extraction equilibrium of Np(VI), U(VI), Pu(IV), HNO_3 and TBP are as follows:

$$NpO_2{}^{2+}{}_{aq} + 2\ NO_3{}^-{}_{aq} + 2\ TBP_{org} \overset{K_{Np(VI)}}{<--->} NpO_2(NO_3)_2(TBP)_{2\ org} \qquad (IV-1)$$

$$UO_2{}^{2+}{}_{aq} + 2\ NO_3{}^-{}_{aq} + 2\ TBP_{org} \overset{K_{U(VI)}}{<--->} UO_2(NO_3)_2(TBP)_{2\ org} \qquad (IV-2)$$

$$Pu^{4+}{}_{aq} + 4\ NO_3{}^-{}_{aq} + 2\ TBP_{org} \overset{K_{Pu(IV)}}{<--->} Pu(NO_3)_4(TBP)_{2\ org} \qquad (IV-3)$$

$$H^+{}_{aq} + NO_3{}^-{}_{aq} + TBP_{org} \overset{K_{HNO3}}{<--->} HNO_3TBP_{org}. \qquad (IV-4)$$

The equilibrium constants of reactions (IV-1), (IV-2), (IV-3) and (IV-4) are defined as:

$$K'_{Np(VI)} = y_{Np(VI)}K_{Np(VI)} = \frac{[NpO_2(NO_3)_2(TBP)_2]_{org}}{[NpO_2^{2+}]_{aq}[NO_3^-]_{aq}^2\ [TBP]_{org}^2} \qquad (IV\text{-}5)$$

$$K'_{U(VI)} = y_{U(VI)}K_{U(VI)} = \frac{[UO_2(NO_3)_2(TBP)_2]_{org}}{[UO_2^{2+}]_{aq}[NO_3^-]_{aq}^2\ [TBP]_{org}^2} \qquad (IV\text{-}6)$$

$$K'_{Pu(IV)} = y_{Pu(IV)}K_{Pu(IV)} = \frac{[Pu(NO_3)_4(TBP)_2]_{org}}{[Pu^{4+}]_{aq}[NO_3^-]_{aq}^4.[TBP]_{org}^2} \qquad (IV\text{-}7)$$

$$K'_{HNO_3} = y_{HNO_3}K_{HNO_3} = \frac{[HNO_3TBP]_{org}}{[H^+]_{aq}[NO_3^-]_{aq}[TBP]_{org}} \qquad (IV\text{-}8)$$

where, K' are apparent equilibrium constants, y are correlation coefficients which includes activity coefficients of the ions. The uncomplexed (free) TBP concentration in Eqs.(IV-5)~(IV-8) is given by subtracting organic concentrations of nitrates from initial concentration of TBP as:

$$[TBP]_{org} = [TBP]_{init} - [HNO_3]_{org} - 2\ \Sigma\ [M]_{org} \qquad (IV\text{-}9)$$

where $[TBP]_{init}$ and $[M]$ are initial concentration of TBP (30 Vol.% TBP is equivalent to 1.096 mol/l) and actinide ion concentration, respectively. Nitric acid ion concentration in aqueous phase is equal to the total concentration of NO_3^- and given as:

$$[NO_3^-]_{aq} = [HNO_3]_{aq} + \Sigma\ m[M]_{aq} \qquad (IV\text{-}10)$$

where m is valence of the actinide ions. The coefficients of each component, y, correlates with ionic strength by second order polynomial functions as:

$$\log K' = a\mu^2 + b\mu + c\mu^{1/2} + d \qquad (IV\text{-}11)$$

where μ is an ionic strength of aqueous phase defined as:

$$\mu = 1/2\ ([NO_3^-]_{aq} + [H^+]_{aq} + \Sigma\ m^2 [M]_{aq}). \qquad (IV-12)$$

The coefficient y was assumed to be not depend on temperature. The parameters of the polynomial function, a, b, c and d, were determined from the distribution equilibrium data between aqueous solutions and TBP for whole temperature range. A non-linear least squares method was used in order to determine the parameters in these regressions[14].

IV-2-2. Results and Discussion

Table IV-1 shows the experimental conditions for the regression. The experimental error of the each data was unknown, but outliers selected by Petrich were not used for the correlations. **Table IV-2** shows the parameters of the correlation and their errors of Eq.(IV-11) estimated by this work. The errors of root mean square were independent of the parameters a for Np(VI), HNO_3 and U(VI). **Figures IV-1**, **IV-2**, **IV-3** and **IV-4** show the relationships between the logarithm of K' and ionic strength for Np(VI), U(VI), Pu(IV) and HNO_3, respectively. Curves in the figures are similar to a change of the activity coefficient of electrolyte solutions. **Table IV-3** shows the sum of squares of difference of the experimental distribution coefficients from the fitting ones for this work and the Richardson's one. The distribution coefficients calculated by this estimation equations for the equilibrium constants are better agreement with the experimental ones than those calculated by the Richardson's. .

Table IV-1 Acid concentration and temperature range of distribution equilibrium data used the regressions

System	Number of data sets	Acid concentration range (mol/l)	Temperature range (°C)
HNO_3-Np(VI)-TBP	194	0 - 11.0	
HNO_3-TBP	172	0 - 9.1	15 - 70
HNO_3-U(VI)-TBP	420	0 - 6.1	20 - 70
HNO_3-Pu(IV)-TBP	83	0 - 7.5	20 - 70

Table IV-2 Parameters and their errors of Eq.(IV-11)

Components	*a*	*b*	*c*	*d*
Np(VI)		1.19×10^{-1}	1.54×10^{0}	-9.14×10^{-1}
		$\pm3.06\times10^{-2}$	$\pm1.02\times10^{-1}$	$\pm8.24\times10^{-2}$
HNO_3		3.10×10^{-1}	-9.59×10^{-1}	-1.35×10^{-2}
		$\pm1.98\times10^{-2}$	$\pm5.57\times10^{-2}$	$\pm3.59\times10^{-2}$
U(VI)		5.61×10^{-1}	-1.31×10^{0}	1.72×10^{0}
		$\pm4.50\times10^{-2}$	$\pm1.49\times10^{-1}$	$\pm1.18\times10^{-1}$
Pu(IV)	-4.87×10^{-2}	1.82×10^{0}	-5.24×10^{0}	4.06×10^{0}
	$\pm8.25\times10^{-3}$	$\pm1.58\times10^{-1}$	$\pm3.20\times10^{-1}$	$\pm1.57\times10^{-1}$

Table IV-3 Sum of squares of difference of the experimental distribution coefficients from the fitting ones

System	this work	Richardson
HNO_3	2.24×10^{-3}	7.11×10^{-2}
U(VI)	1.73×10^{1}	5.60×10^{1}
Pu(IV)	1.30×10^{1}	2.28×10^{0}
Np(VI)	5.41×10^{0}	

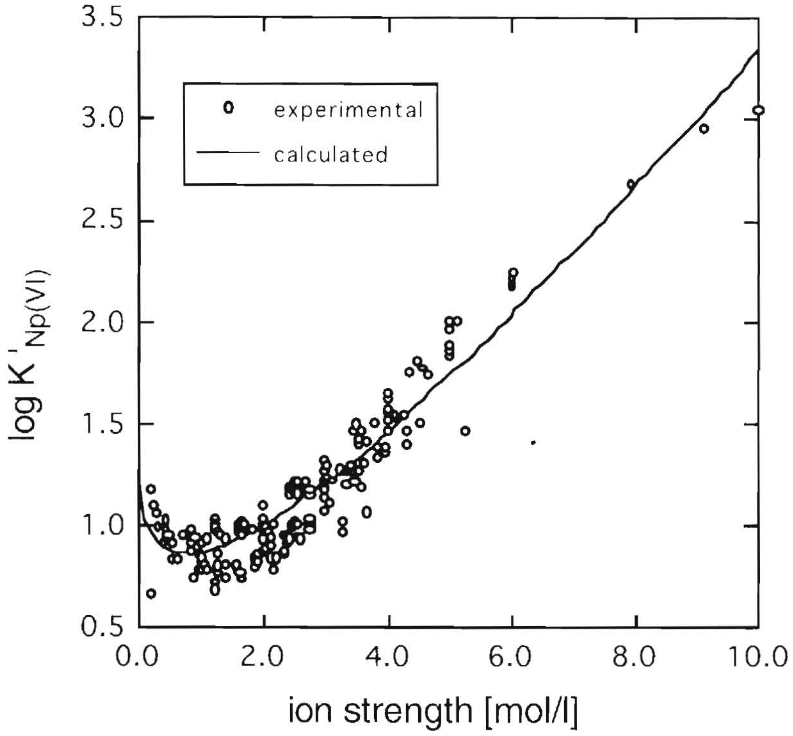

Fig.IV-1 Relationship between logarithm of *K'* and total ionic strength for Np(VI)

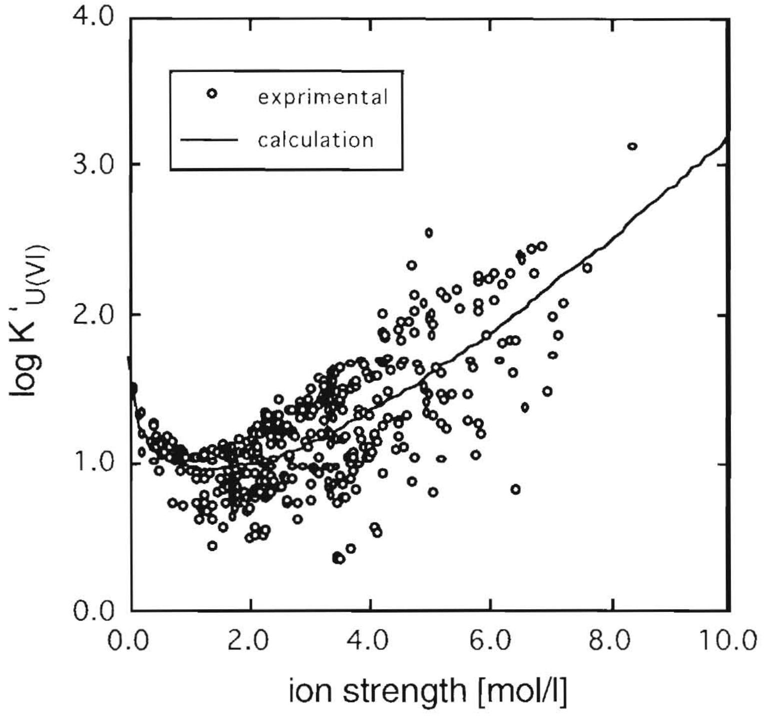

Fig.IV-2 Relationship between logarithm of *K'* and total ionic strength for U(VI)

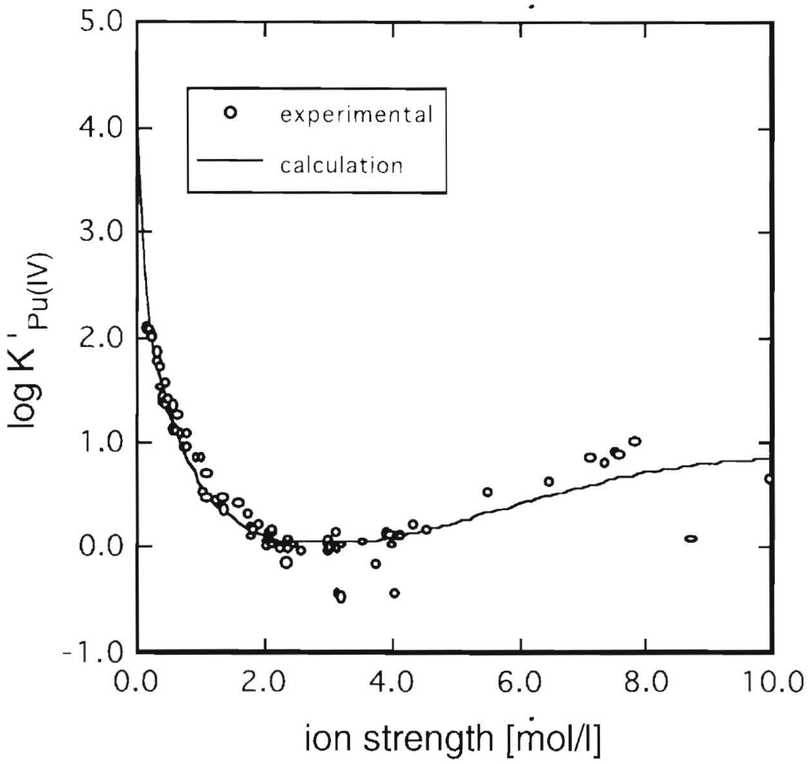

Fig.IV-3 Relationship between logarithm of *K'* and total ionic strength for Pu(IV)

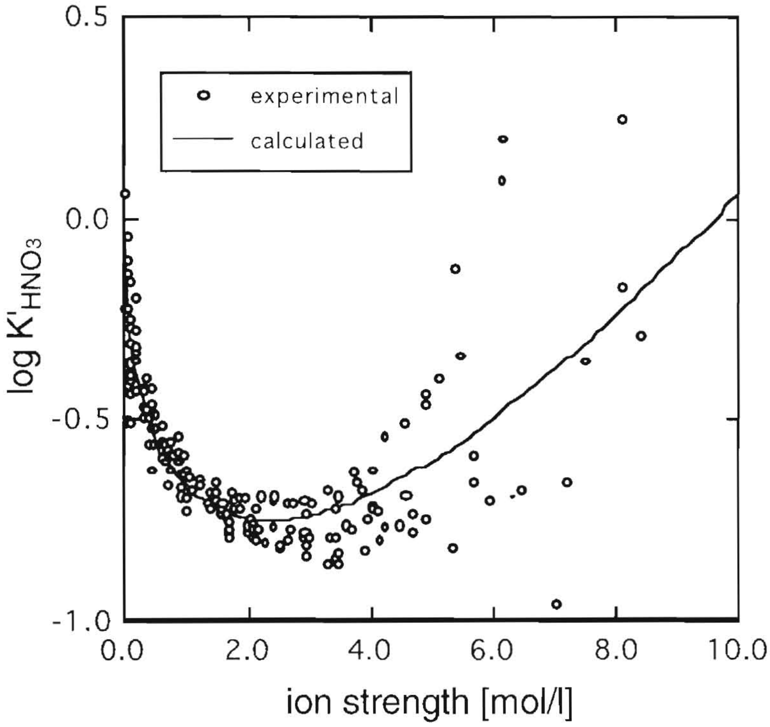

Fig.IV-4 Relationship between logarithm of *K'* and total ionic strength for HNO_3

IV-3. Oxidation-Reduction Reactions Concerning with Neptunium

Since the extraction and the oxidation-reduction reactions occur in the extraction process simultaneously, the reaction kinetics of neptunium affect its behavior in the process. Particularly, the extraction behavior in the co-decontamination process determines whether neptunium is coextracted with uranium and plutonium to the product stream or not extracted and flows to the waste stream. In this section, the oxidation-reduction reactions concerning with neptunium in the co-decontamination process are collected from the presented literatures. Their reaction rate equations are also given here.

IV-3-1. Disproportionation Reaction of Neptunium

Pentavalent neptunium disproportionates to tetra and hexa valent ones in the nitric acid solution as:

$$2\ NpO_2^{+} + 4\ H^{+} \longleftrightarrow NpO_2^{2+} + Np^{4+} + 2\ H_2O. \qquad (IV\text{-}13)$$

A reaction rate equation of Eq.(IV-13) has been suggested by Koltunov et al.[15] as:

$$-d[NpO_2^{+}]/dt = 2\ k\ [NpO_2^{+}]^2[H^{+}]^2 \qquad (IV\text{-}14)$$
$$k = 0.113 \pm 0.05\ M^{-3}min^{-1}\ (90\,^{\circ}C).$$

Since the reaction of Eq.(IV-13) includes a structure change from NpO_2^{+} to Np^{4+}, the reaction rate is very slow. This reaction may be neglected under the normal operational condition in the Purex process[16].

IV-3-2. Reduction of Neptunium by Hydrazine

Generally, hydrazine is fed to the U-Pu partition process in order to scavenge nitrous acid which promotes reoxidation of Pu(III). It has been tentatively used at the co-decontamination process in order to control neptunium extraction[17]. Reduction of neptunium by hydrazine, therefore, should be considered for neptunium extraction.

Hexa and penta valent neptunium are reduced by hydrazine. Reduction reaction from Np(VI) to Np(V) occurs in nitric acid solution containing excessive quantity of hydrazine as:

$$2\ NpO_2^{2+} + 2\ N_2H_4 \text{--->} 2\ NpO_2^{+} + 2\ NH_4^{+} + N_2. \qquad (IV\text{-}15)$$

The production rate of Np(V) is described as[18]:

$$d[NpO_2^{+}]/dt = k\ [NpO_2^{2+}][N_2H_4]/[H^{+}]^{1.3} \qquad (IV\text{-}16)$$

$$k = 8.29 \pm 0.05\ M^{-0.7}min^{-1}\ (20^{\circ}C).$$

As showing Eq.(IV-16), this reaction proceeds very rapidly. On the other hand, reduction reaction from Np(V) to Np(VI) occurs as:

$$2\ NpO_2^{+} + 2\ N_2H_4 + 8\ H^{+} \text{--->} 2\ Np^{4+} + 2\ NH_4^{+} + N_2 + 4\ H_2O. \qquad (IV\text{-}17)$$

The rate of the reaction (IV-17) is as slow as the disproportionation reaction of Eq.(IV-13) because of the structure change from NpO_2^{+} to Np^{4+}[19]. This reaction, therefore, may be also neglected under the normal operational condition in the Purex process[16].

IV-3-3. Oxidation-Reduction Reaction of Neptunium by Nitrous Acid

It is known that the extraction behavior of neptunium strongly depends upon nitrous acid concentration. The reaction of neptunium concerning the nitrous acid proceeds as:

$$2\ NpO_2^+ + 3\ H^+ + NO_3^- <\text{--->} 2\ NpO_2^{2+} + HNO_2 + H_2O. \qquad \text{(IV-18)}$$

Several kinetic studies for reaction (IV-18) have been carried out. Siddall et al.[20] have found out that the rate of Np(V) decomposition is proportional to fourth power of hydrogen ion concentration experimentally and proposed a rate equation as:

$$-d[\mathrm{Np(V)}]/dt = k\ [\mathrm{Np(V)}][\mathrm{H}^+]^4. \qquad \text{(IV-19)}$$

On the one hand, Swanson[21] has observed that the rate of Np(V) decomposition is proportional to nitrous acid concentration and independent on nitric acid concentration above 2 M in nitric acid. He has also proposed a rate equation as:

$$-d[\mathrm{Np(V)}]/dt = k\ [\mathrm{Np(V)}][\mathrm{HNO_2}]. \qquad \text{(IV-20)}$$

Recently, Mouline[22] has got a result that the reaction rate depends on nitric acid concentration and a ratio of pentavalent neptunium and nitrous acid concentration as:

$$-d[\mathrm{Np(V)}]/dt = k\ [\mathrm{Np(V)}][\mathrm{H}^+]^{1\ 3}[\mathrm{NO_3^-}]^2(1+[\mathrm{Np(V)}]/[\mathrm{HNO_2}]). \qquad \text{(IV-21)}$$

Though the contradiction of them may result from the difference of experimental condition, these results imply that the behavior of the reaction is very complicated.

According to extraction behavior in the co-decontamination process[17], reaction of Eq.(IV-18) must be a reversible reaction. Eqs.(IV-19), (IV-20) and (IV-21), however, are not considered the reverse reaction of Eq.(IV-18). A rate equation expressed as a reversible reaction, therefore, should be used to simulate the extraction process as:

$$-d[\mathrm{Np(V)}]/dt = k\ \left([\mathrm{Np(V)}]-[\mathrm{Np(V)}]_{eq}\right) \qquad \text{(IV-22)}$$

where, $[Np(V)]_{eq}$ is an equilibrium concentration of Np(V), which calculates the following equation as:

$$K = [Np(VI)]_{eq}[HNO_2^-]_{eq}^{1/2} / [Np(V)]_{eq}[H^+]_{eq}^{3/2}[NO_3^-]_{eq}^{1/2}. \quad (IV-23)$$

An equilibrium constant of Eq.(IV-23) is theoretically calculated from oxidation-reduction potential[23] and is 0.00048 $[(mol/l)^{-3/2}]$. The constant, however, depends upon the concentration of the solution because of deviation from ideal solution. Several apparent equilibrium constants have been obtained experimentally by former researchers[20,21,24,25]. The constants are expressed by the following equation as:

$$K' = [Np(VI)][HNO_2]^{\alpha} / [Np(V)][HNO_3]^{\beta}. \quad (IV-24)$$

Table IV-4 shows the constant and the orders in Eq.(IV-24) presented by the former researches.

The oxidation-reduction reaction of neptunium by nitrous acid is very complicated and the results of the former researches have some contradictions as stated above. In the following chapter, qualitative analysis of this reaction will be carried out based on the observations of neptunium extraction by mixer-settler.

Table IV-4 Apparent equilibrium constants and orders of Eq.(IV-24)

Reference	logK'	α	β
Siddall et al.20)	-3.28±0.09	1/2	2
Gourisse24)	(-3.37~-3.03)±0.05	1/2	2
Swanson21)	-3.57±0.06	1/2	3
	-3.13±0.04	1/2	2
Tanaka et al.25)	-2.92±0.05	1/3	3

IV-4. Conclusion

The new estimation equation of the distribution coefficient for Np(VI) was proposed. The estimation equations for the distribution coefficients of U(VI), Pu(IV) and nitric acid were also remade. These estimation equations have equilibrium constants which correlate with the total ionic strength in the aqueous phase. The parameters correlated by the non-linear least squares method were obtained for every component. Distribution coefficients estimated by these equations were in good agreement with the presented distribution data.

The oxidation-reduction reactions for neptunium in the nitric acid solution were briefly summarized. In co-decontamination process, principal reaction for neptunium is the oxidation-reduction reaction by nitrous acid. This reaction has not been well understood, a quantitative analysis of this reaction, therefore, will be carried out in the next chapter.

References

1) Alcock, K., Grimley, S.S., Healy, T.V, Kennedy, J., McKay, H.A.C.: "The Extraction of Nitrates by Tri-n-butyl Phosphate (TBP), Part 1. The System TBP + Diluent + H_2O + HNO_3", *Trans.Faraday Soc.*, **52**, 39 (1956).

2) Hesford, E., McKay, H.A.C.: "The Extraction of Nitrates by Tri-n-butyl Phosphate (TBP), Part 3. Extraction at Trace Concentrations", *ibid.*, **54**, 573 (1958).

3) Jenkins, I.L., McKay, H.A.C.: "The Partition of Uranyl Nitrate between Water and Organic Solvents, Part 6. Salting-Out by a Second Nitrate", *ibid.*, **50**, 107 (1954).

4) Marcus, Y.: "Extraction of Tracer Quantities of Uranium(VI) from Nitric Acid by Tri-n-butyl Phosphate", *J.Phys.Chem.*, **65**, 1647 (1961).

5) Collopy, T.J., Cavendish, J.H.: "Equilibrium Constant for the System Tri-n-Butyl Phosphate-Water-Nitric Acid", *ibid.*, **64**, 1328 (1960).

6) Goldberg, S.M., Benedict, M., Levi, H.W.: "Distribution of Uranyl Nitrate and Nitric Acid between Aqueous Solutions and 30 Volume Percent Tributyl Phosphate in Hydrocarbon Diluent", *Nucl.Sci.Eng.*, **47**, 169 (1972).

7) Horner, D.E.: "A Mathematical Model and A Computer Program for Estimating Distribution Coefficients for Plutonium, Uranium and Nitric Acid with Tri-n-butylphosphate", *ORNL-TM*-2711 (1970).

8) Naito, K.: "On the Mechanism of the Extraction of Uranyl Nitrate by TBP", *Bull.Chem.Soc.Jpn.*,**33**(3), 363 (1960).

9) Nishi, T., Asano, M.: "Extraction Equilibrium of Nitric Acid by TBP[3]", *J.Chem.Soc.Japan, Ind.Chem.Sect.*(in Japanese), **66**, 1424 (1963).

10) Nishi, T., Asano, M.: "Thermodynamic Values of Uranyl Nitrate and Nitric Acid Extraction by Organophosphorus Compounds[4]", *ibid.*(in Japanese), **66**, 1428 (1963).

---

[3] Translation from Japanese title.

[4] Translation from Japanese title.

11) Olander, D.R., Donadieu, L., Benedict, M.: "The Distribution of Nitric Acid between Water and Tributyl Phosphate-Hexane Solvents", *A.I.Ch.E.J.*, **7**, 152 (1961).

12) Richardson, G.L., Swanson, J.L.: "Plutonium Partitioning in the Purex Process with Hydrazine-Stabilized Hydroxylamine Nitrate", *HEDL-TME*-7531 (1975).

13) Petrich, G., Kolarik, Z.: "The 1981 Purex Distribution Data Index", *KfK*3080 (1981).

14) Press, W.H., Flannery, B.P., Teukolsky, S.A., Vetterling, W.T.:"Numerical Recipes", pp.307~312 (1986), Cambridge Univ.Press, New York.

15) Koltunov, V.S., Rykov, A.G.: "Latest Achievements in the Field of the Investigation of the Kinetics and Mechanism of Redox Reactions of Neptunium and Plutonium", *Radiokhimiya*, **18**, 34 (1976).

16) Guillaume, B., Mouline, J.P., Maurice, C.: "Chemical Properties of Neptunium Applied to Neptunium Management in Extraction Cycles of Purex Process", *I.Chem.E.Symp.Series* 88, 31(1984).

17) Tsuboya, T., Tanaka, T., Nemoto, S., Hoshino, T.: "Some Modifications of a Purex Process for the Recovery of Neptunium", *Proc.ISEC* '74, vol.3, 1985 (1974).

18) Koltunov, V.S., Tikhonov, M.F.: "Kinetics of Reduction of Neptunium by Hydrazine, II. Reduction of Np(VI) to Np(V) in Nitric Acid", *Radiokhimiya*, **15**, 194 (1973).

19) Koltunov, V.S., Marchenko, V.L., Zhuravleva, G.I., Tikhonov, M.F., Shapovalov, M.P.: "Kinetics of the Reactions of Oxidation of Np(IV) by Pu(IV), Fe(III) and V(V) ions and the reduction of Np(V) by Hydrazine", *ibid.*, **18**, 65 (1976).

20) Siddall, T.H. III, Dukes, E.K.: "Kinetics of HNO_2 Catalyzed Oxidation of Neptunium(V) by Aqueous Solutions of Nitric Acid", *J.Am.Chem.Soc.*, **81**, 790 (1959).

21) Swanson, J.L.: "Oxidation of Neptunium(V) in Nitric Acid Solution - Laboratory Study of Rate Accelerating materials (RAM)", *BNWL*-1017, (1969).

22) Mouline, J.P.: "Oxidation-Reduction Kinetics of Neptunium

in Nitric Acid Solution", *CEA-R*-4665, (1975).

23) Benedict, M., Pigford, T.H., Levi, H.W.: "Nuclear Chemical Engineering", (1981), McGraw-Hill.

24) Gourisse, D.: "Oxidation of Np(V) by Aqueous Solutions of Nitric Acid in the Presence of Nitrous Acid", *J.Inorg.Nucl.Chem.*, **33**, 831 (1971).

25) Tanaka, T., Nemoto, S., Tsuboya, T., Hoshino, T.: "Neptunium Recovery in the Purex Process. (II), Np Behaviour in a Purex Codecontamination Cycle with Nitrous Acid", *PNCT*-841-71-35(in Japanese), (1971).

CHAPTER V

ANALYSIS OF OXIDATION-REDUCTION REACTION BETWEEN Np(V) AND Np(VI) BY NITROUS ACID

V-1. Introduction

Neptunium is one of the important nuclide in the Purex process. Its behavior in the process is very complicated as stated the former chapter. The reasons are summarized below as:

i) Three valences of IV, V and VI are observed in nitric acid solution.
ii) Tetra and hexa valent neptunium are extracted by TBP, but pentavalent is not extracted.
iii) Its valency and their distribution coefficients are strongly dependent on the concentration of the solutions.

Simulation of its behavior, therefore, requires both data of extraction equilibria between organic and aqueous solution and oxidation-reduction reactions in the nitric acid solution. In the former chapter, it is shown that the qualitative assessment of the oxidation-reduction reaction between Np(V) and Np(VI) by nitrous acid is not enough to simulate the neptunium behavior. In this chapter, the qualitative analysis of the oxidation-reduction reaction between Np(V) and Np(VI) by nitrous acid is carried out to develop the rate equation of the reaction used for the simulation of neptunium extraction behavior. The rate equation used in this analysis is the same equation as Eq.(IV-22). The rate constant in Eq.(IV-22) and the equilibrium constant in Eq.(IV-23) were determined to minimize the difference between the experimental concentration profiles of neptunium and simulated one. For the analysis, a new approach building the simulation codes is also suggested to easily extend the multi-component extraction system. This approach is expected to the analysis of some reaction kinetics for other components except neptunium.

V-2. Extraction Model

For multi-component extraction system, a simulation code includes a lot of equations, which calculate the distribution coefficients and reaction rates. Generally, these equations are non-linear functions depending on the solute concentrations. If a usual approach is used to build the simulation code, the calculation results, such as concentration profiles, are not solved because of their non-linearities. Thus, simplification of the extraction model is required for the multi-component extraction system without lack of accuracy.

Figure V-1 shows the concept of this extraction model, which is simplified the expression of the reactions. All oxidation-reduction reactions are assumed to occur only in aqueous phase shown in the figure. Solute concentration in organic phase, shaded area in the figure, is in equilibrium state with that of aqueous one. Now, this model is applied to the extraction process with mixer-settler type contactor. Mass balance in one stage of the mixer-settler is expressed as:

$$Q_{x,\ \mathrm{in}} x_{\mathrm{in},\ j} + Q_{y,\ \mathrm{in}} y_{\mathrm{in},\ j} + V r_j = Q_{x,\ \mathrm{out}} x_{\mathrm{out},\ j} + Q_{y,\ \mathrm{out}} y_{\mathrm{out},\ j} \qquad \text{(V-1)}$$

$$D_j = y_{\mathrm{out},\ j} \ /\ x_{\mathrm{out},\ j} \qquad \text{(V-2)}$$

where,

D = distribution coefficients

Q = volumetric flow rate
r = reaction rates
V = reaction volume
x = solute concentration in aqueous phase
y = solute concentration in organic phase

Subscripts represent,

in = inlet
out = outlet
x = aqueous phase
y = organic phase
j = component.

The distribution coefficients of Np(VI), HNO_3, U(VI) and Pu(IV) are calculated by the estimation equations established in the former chapter[1]. That of HNO_2 is estimated from the distribution data reported by Bähr and Hotoku et al.[2,3]. It is also assumed that penta valent neptunium and hydrazine are not extracted by TBP. The computer program for simulation of extraction behavior in co-decontamination process was implemented by using of a COMPAS flowsheeting system[4].

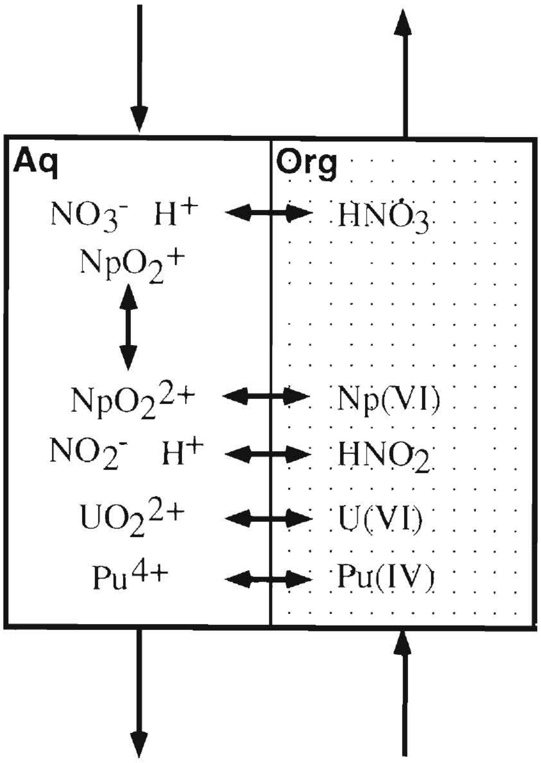

Fig.V-1 Concept of the extraction model (oxidation-reduction reactions in organic phase are not considered.)

V-3. Results and Discussion

The rate equation of the oxidation-reduction reaction between Np(V) and Np(VI) by nitrous acid is shown again as:

$$-d[\mathrm{Np(V)}]/dt = k\left([\mathrm{Np(V)}]-[\mathrm{Np(V)}]_{eq}\right) \qquad \text{(V-3)}$$

where, $[\mathrm{Np(V)}]_{eq}$ is an equilibrium concentration of Np(V), which calculates the following equation as:

$$K = [\mathrm{Np(VI)}]_{eq}[\mathrm{HNO_2}^-]_{eq}^{1/2}/[\mathrm{Np(V)}]_{eq}[\mathrm{H^+}]_{eq}^{3/2}[\mathrm{NO_3}^-]_{eq}^{1/2}. \qquad \text{(V-4)}$$

In this study, the rate and equilibrium constants in Eqs.(V-3) and (V-4) were determined by using the results of neptunium extraction experiments presented in open literature. Determination of the constants was carried out by a non-linear least squares method[5].

Tsuboya et al.[6] carried out some experiments of neptunium extraction in the co-decontamination process controlled by nitrous acid concentration. **Figures V-2** (Run 1) and **V-3** (Run 2) show their flowsheets by using of the mixer-settler with 16-stage. For both experiments of Run 1 and 2, Np(V) and Np(VI) were fed to 8-th stage. Organic solvent of 30%-TBP/dodecane and scrub solution of nitric acid were supplied to first and 16-th stages, respectively. Sodium nitrite was supplied in order to control nitrous acid concentration to third stage for Run 1 and to first stage for Run 2, respectively. For only Run 2, hydrazine was supplied to 8-th stage in order to scavenge nitrous acid as[7]:

$$N_2H_5^+ + HNO_2 \dashrightarrow H^+ + HN_3 + 2\ H_2O \qquad (V-5)$$

$$HN_3 + HNO_2 \dashrightarrow N_2O + N_2 + H_2O. \qquad (V-6)$$

Reduction reactions of Np(VI) and Np(V) by hydrazine are not considered in the simulation, because all hydrazine fed to 8-th stage are consumed by the rapid reactions with nitrous acid as shown in Eqs.(V-5) and (V-6).

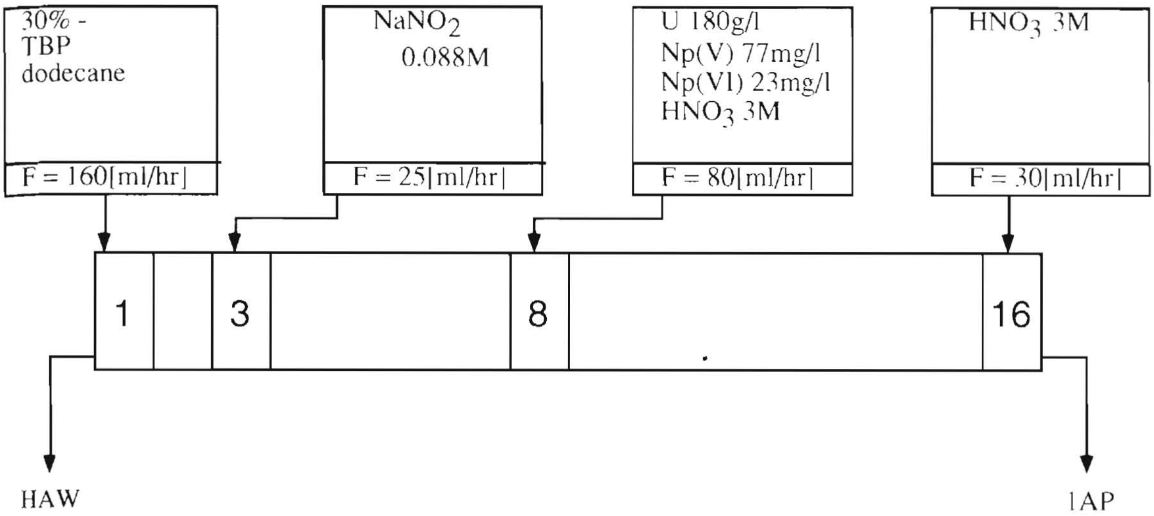

Fig.V-2 Flowsheet of Np extraction in co-decontamination process (Run 1)

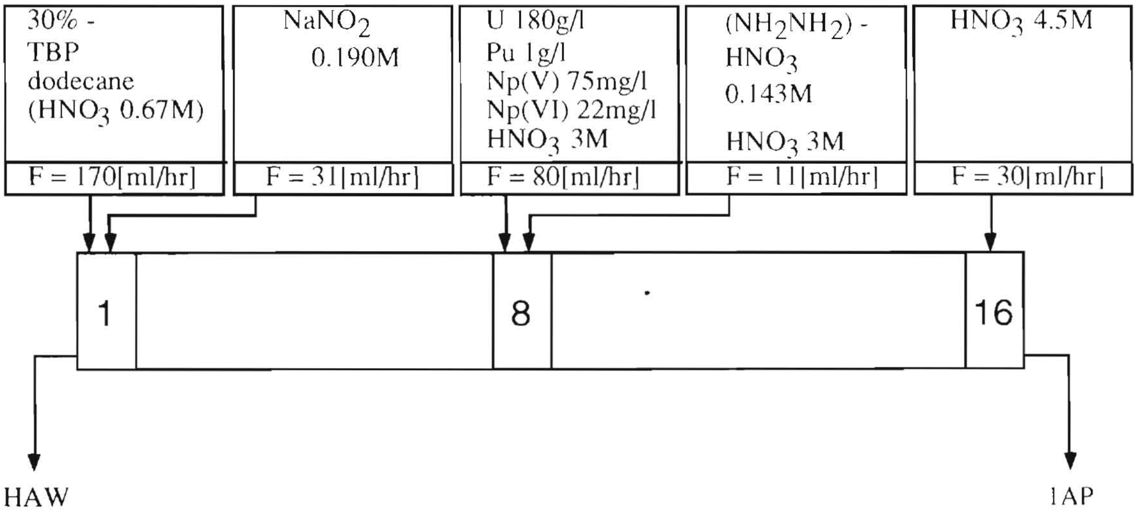

Fig.V-3 Flowsheet of Np extraction in co-decontamination process, used by hydrazine as scavenger of nitrous acid (Run 2)

Figure V-4 shows the comparison between experimental and calculated concentration profiles of total neptunium for Run 1. Both aqueous and organic concentration profiles have a peak at 8-th stage. The peak of neptunium concentration results from influence of nitrous acid[8]. Calculated profiles by this model are well simulated the peak and in good agreement with experimental ones. In case of supplying hydrazine (Run 2), the peak of neptunium concentration was not found as shown in **Fig.V-5**. It was assumed that nitrous acid in the stage was consumed equivalent of hydrazine according to Eq.(V-5) in the simulation of Run 2. Both aqueous and organic concentration profiles of neptunium calculated by this model are also in good agreement with experimental ones.

Table V-1 shows the determined reaction rate constant and equilibrium one in Eqs.(V-3) and (V-4). The errors of their constants are also shown in the table. The rate constant and the equilibrium one for Run 1 are in agreement with those for Run 2 in consideration of their errors. Logarithmic values of the equilibrium constants are well agreement with the presented values by the former researchers as shown in the Table IV-4. The determined rate equation, therefore, is adequate for the simulation of neptunium extraction behavior.

Table V-1 The rate and the equilibrium constants in Eqs.(V-3) and (V-4) determined from neptunium concentration profiles of Run 1(Fig.V-4) and Run 2(Fig.V-5)

	Run 1 Fig.V-4	Run 2 Fig.V-5
k $[\mathrm{min}^{-1}]$	$1.25\times10^{-2}\pm2.51\times10^{-3}$	$1.97\times10^{-2}\pm4.47\times10^{-3}$
K $[(\mathrm{l/mol})^{3/2}]$	$6.04\times10^{-4}\pm7.17\times10^{-5}$	$11.5\times10^{-4}\pm5.03\times10^{-4}$
$\log K$	-3.22	-2.94

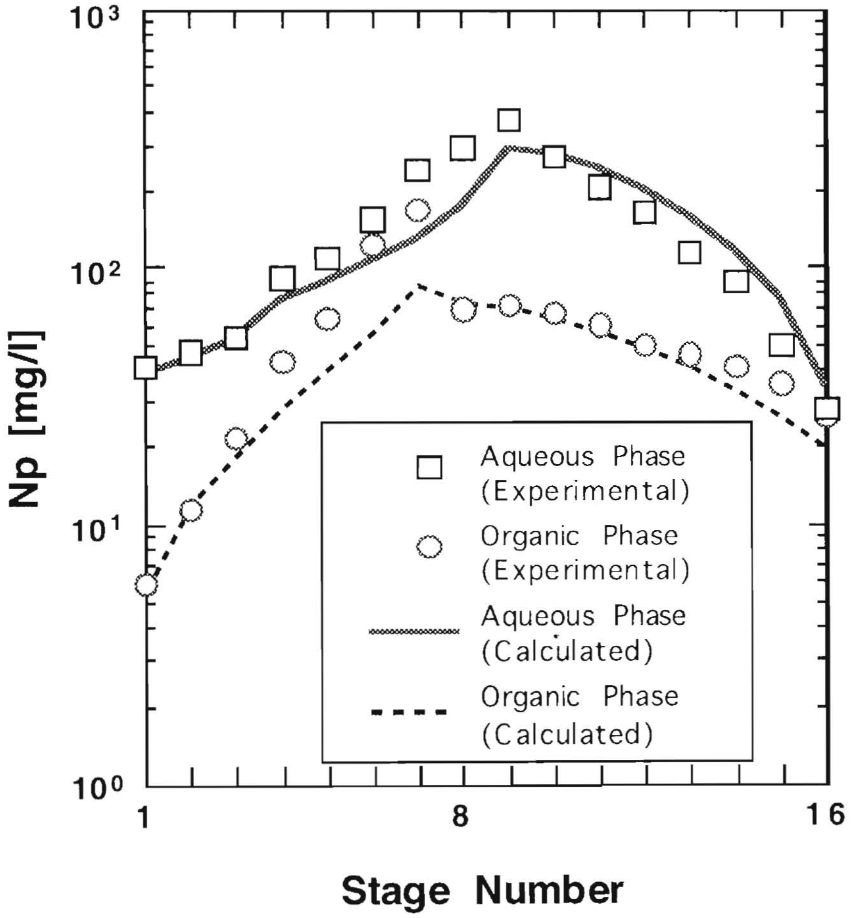

Fig.V-4 Comparison between simulated and experimental concentration profiles of Np in Run 1

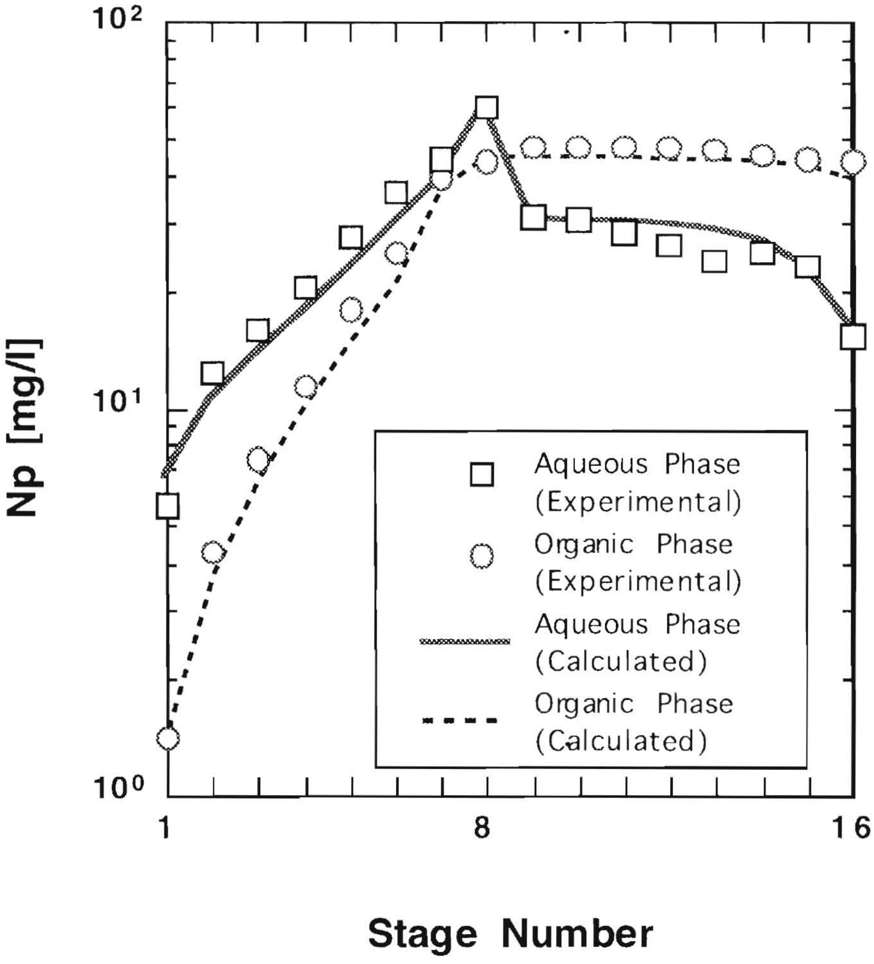

Fig.V-5 Comparison between simulated and experimental concentration profiles of Np in Run 2

V-4. Conclusion

The qualitative analysis of the oxidation-reduction reaction between Np(V) and Np(VI) with nitrous acid was carried out and the rate equation of the reaction was developed. The simulation results based on the developed rate equation were compared with the experimental results for neptunium behavior in the co-decontamination process. The simulated concentration profiles of neptunium were fairly well agreement with experimental ones. Determined rate constant and equilibrium one, therefore, are adequate to simulate the neptunium extraction behavior.

For the analysis, a new approach building the simulation code was also suggested to easily extend the multi-component extraction system. All oxidation-reduction reactions in this model are assumed to occur only in aqueous phase. This model should be applicable to the simulation of other components except uranium and plutonium. The approach in this study, which determines reaction rate equation from the extraction experiments, should be available for the analysis for the reaction kinetics of other components in the Purex extraction process.

References

1) Homma, S., Takanashi, M., Koga, J., Matsumoto S.: "Estimation of Distribution Coefficients of U(VI), Pu(IV) and Np(VI) in HNO_3-30%TBP/n-alkane System", *Sci.Eng.Reports Saitama Univ.*, **27**, 5 (1993).
2) Bähr, W.: "Das Extractionsverhalten von Neptunium bei der Wiederaufarbeitung von Bestrahalten Kernbrennstoffen nach dem Purex-Prozess", *KfK*-797(in German), (1968).
3) Hotoku, S., Kihara, T., Uchiyama, G., Fujine, S., Maeda, M.: "Distribution Equilibrium of Nitrous Acid in Reprocessing solution", *JAERI-M* 93-095(in Japanese), (1993).
4) Homma, S., Sakamoto, S., Takanashi, M., Nammo, A., Satoh, Y., Soejima, T., Koga, J., Matsumoto S.: "Development of COMPAS, Computer Aided Process Flowsheet Design and Analysis System of Nuclear Fuel Reprocessing", *J.Nucl.Sci.Tecnol.* (in press).
5) Press, W.H., Flannery, B.P., Teukolsky, S.A., Vetterling, W.T.:"Numerical Recipes", pp.307~312 (1986), Cambridge Univ.Press, New York.
6) Tsuboya, T., Tanaka, T., Nemoto, S., Hoshino, T.: "Some Modifications of a Purex Process for the Recovery of Neptunium", *Proc.ISEC* '74, vol.3, 1985 (1974).
7) Perrott, J.R., Stedman, G., Uysal, N.: "Kinetic and Product Study of the Reaction between Nitrous Acid and Hydrazine", *J.Chem.Soc., Dalton Trans.*, 2058 (1976).
8) Tanaka, T., Nemoto, S., Tsuboya, T., Hoshino, T.: "Neptunium Recovery in the Purex Process. (II), Np Behaviour in a Purex Codecontamination Cycle with Nitrous Acid", *PNCT-841-71-35*(in Japanese), (1971).

CHAPTER VI

FLOWSHEET CALCULATION OF PUREX PROCESS

VI-1. Introduction

In the research and development for the Purex process, flowsheet calculations are required for: i) Determination of operational conditions, ii) Verification of the applicability for the modified or newly developed process, and iii) Estimation of waste volume and its composition. Moreover, a flowsheet calculation system is strongly desired for the researches and developments having the view point of the safety and the waste minimization.

Several flowsheet calculation programs for design and simulation of the general chemical process have been on the market[1]. Some of them could be also used for design and operation of the nuclear fuel reprocessing. REPROCX[2] have been developed as a flowsheet calculation system for the reprocessing process in order to facilitate linking several established simulation codes. It also contains a plenty of knowledge and experiences of U.K. fuel reprocessing. The REPROCX, however, would be unsuitable to modify the process structure easily.

A COMPAS (**COM**puter aided **P**rocess flowsheet design and **A**nalysis **S**ystem for nuclear fuel reprocessing) system[3] is developed as the flowsheet calculation tool. This system can be used not only the process flowsheet calculation but also the modification of the flowsheet as user's wishes can be done. Outline of the COMPAS system and its application are shown in this chapter. An example of the application is determination of operational condition for flow control of neptunium in the Purex process. A simulation code used in the example was developed based on the results in the former chapters.

VI-2. Summary of COMPAS

Major aim of developing the COMPAS is realization of below three functions to unite the basic algorithms for flowsheet calculation[4] and the Graphical User Interface (GUI):

i) Easily making flowsheet diagram on graphical display.
ii) Directly obtaining the information of equipments and the calculated results in the streams connected between the equipments on the display.
iii) Sharing the simulation codes and other information on the computer network with both researchers and engineers.

A prototype of the flowsheet calculation system based on the above strategies have been developed in 1991[5]. The COMPAS is an improved system of the prototype to deal with the nuclear fuel reprocessing.

All of equipments, such as a dissolver, a mixer-settler, and so on, in the process flowsheet diagram are graphically visualized as icons on a bitmap display of UNIX workstation. Drawing of a flowsheet can be carried out easily by the mouse operation. Not only a published simulation code but also a user's original one can be used on the COMPAS. At present, several simulation codes, which are for the simulation of spent fuel composition, a shearing machine, a dissolver, a feed controller, a mixer-settler and a pulsed column, can be used on the COMPAS. Specifications of the equipments and the concentration of components in the stream displayed as tables can be edited by a computer user. Results of calculation can be also displayed graphically.

VI-3. Determination of Operational Condition for Neptunium Flow Control

One of interesting problems for treatment of TRU elements is how to separate neptunium from other elements. Three strategies in the Purex process can be considered as:

(1) After making Np accompany with the highly active waste (HAW) stream from the co-decontamination process, Np is separated from the waste.

(2) After making Np accompany with U-product at U-Pu partition process, Np is separated from the product or recycled as fuel with uranium.

(3) After making Np accompany with Pu-product at U-Pu partition process, Np is recycled as the MOX fuel with plutonium.

Second and third strategies may be acceptable ways to manage neptunium, because some additional processes are not required in contrast with first strategy and it may be possible that neptunium is kept into closed fuel cycle. In this study, determination of operational condition for control of neptunium flow is carried out based on the second and third strategies.

It is well known that neptunium has three valences of IV, V and VI in nitric acid solution under normal Purex extraction condition. It is also known that Np(IV) and Np(VI) are extracted by TBP, but Np(V) is not extracted. Behavior of Np extraction, therefore, is complicated because its valence is affected by oxidation reduction reactions with other components in the solution. It is necessary for efficient Np separation to control its valence by a proper way.

Before determination of operational conditions, the flowsheet of the Purex process and an original simulation code for Np extraction must be prepared. **Figure VI-1** shows the Purex process flowsheet on the COMPAS. The flowsheet consists of a power reactor, a shearing machine, a batch dissolver, a feed controller and four banks of mixer-settler. Icon of No.4 represents the spent fuel shipped from the power reactor. Input icons, No.0, 1, 2 and 3, represent feed of scrub, solvent to co-decontamination and U-Pu partition process, and strip solution, respectively. Output icons represent off-gas(No.8 and 9), HAW(No.15), Pu-product(No.20) and U-product(No.21). Two recycled loops, which are sets of streams; (11, 13, 12) and (17, 18, 16, 19), can be found on the flowsheet. After drawing the flowsheet by the mouse operation, the variables of input and specifications of the units are edited in the icons. The original code for Np extraction have been developed to incorporate Np distribution data and the rate equations concerning Np reactions as stated in the former chapters.

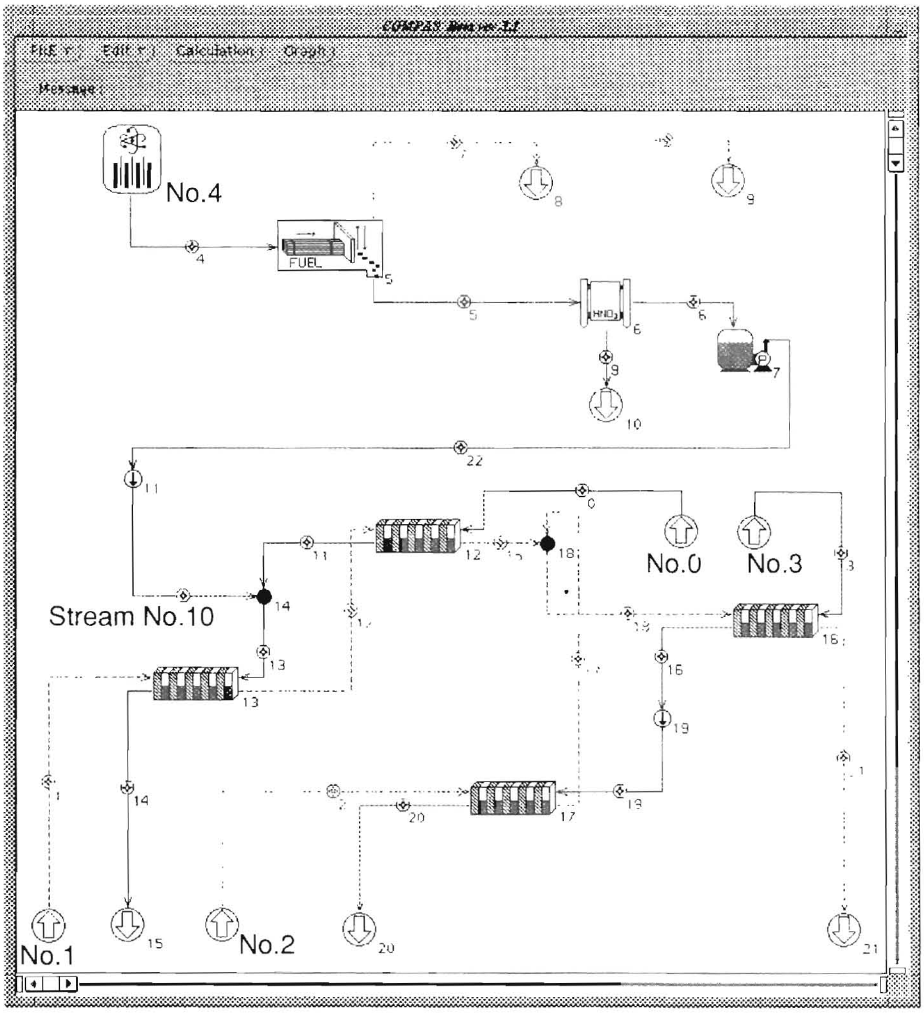

Fig.VI-1 Purex process flowsheet on the COMPAS

To achieve the second and third strategies, it is desirable that all neptunium into the co-decontamination process are carried to the U-Pu partition one. Simulation of finding the desirable operational condition were attempted. The goal of the simulation is that neptunium is transferred to the next partition process as much as possible to control the organic solvent feed rate into the co-decontamination process shown as the input icon No.1 in the Fig.VI-1. Two banks of mixer-settler are used for the co-decontamination process in our example flowsheet. One bank composed 5 stages is for the scrub, the other bank composed 10 stages is for the extraction. Volume of one stage for the scrub and the extraction banks are 2.0×10^{-2} and 3.0×10^{-2} m^3, respectively. **Table VI-1** shows the feed conditions after the feed controller shown the stream icon No.10 in the Fig.VI-1. Generation of neptunium in 3.0% ^{235}U-enriched PWR fuel is calculated by ORIGEN2[6] for burn-up of 20,000, 30,000 and 40,000 MWd/U-ton, respectively. The concentration of U(VI) fed into the co-decontamination process is fixed for 250 g/l. On the other hand, the concentration of Pu(IV) and Np are changed with their generation in the power reactor. Concentration ratio of Np(VI) and Np(V), [Np(VI)]/[Np(V)] is 0.43 fixed for the respective burn-up. Concentration of nitric and nitrous acid are fixed for 3.0 and 2.0×10^{-2} mol/l, respectively. **Table VI-2** shows the feed conditions of aqueous scrub and strip solution in the input icon No.0 and 3 in the Fig.VI-1, respectively.

Table VI-1 Flow rates and feed concentrations into co-decontamination process

Burn-up	[MWd/Ut]	20,000	30,000	40,000
Flow rate	[m^3/h]	5.0×10^{-2}	5.0×10^{-2}	5.0×10^{-2}
U(VI)	[g/l]	250.0	250.0	250.0
Pu(IV)	[g/l]	1.85	2.38	3.20
Np(V)	[g/l]	5.05×10^{-2}	1.09×10^{-1}	1.92×10^{-1}
Np(VI)	[g/l]	2.16×10^{-2}	4.67×10^{-2}	8.25×10^{-2}
HNO_3	[mol/l]	3.0	3.0	3.0
HNO_2	[mol/l]	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Table VI-2 Flow rates and concentrations in scrub and strip solutions

		Scrub solution	Strip solution
Input icon in Fig.VI-1		No.0	No.3
Flow rate	[m^3/h]	5.0×10^{-2}	3.2×10^{-2}
HNO_3	[mol/l]	3.0	2.0
U(IV)	[g/l]	-	71.4
Hydrazine	[mol/l]	-	0.5

The simulations varied the feed rate of organic solvent in the input icon No.1 in the Fig.VI-1 are carried out for the respective burn-up condition. **Figure VI-2** shows the relationships between Np recovery and flow rate of the organic solvent. The recovery is defined as the fraction of neptunium recovered into the following U-Pu partition process to the total neptunium fed into the co-decontamination process. When all neptunium recover to the partition process, the recovery is 100 %. According to the figure, the recovery increases with the flow rate of the solvent, and it does not depend on the burn-up of the fuel. The results show that control of organic solvent feed rate is one of available way to realize the second and third strategies for our example. It is kept in mind that the control of neptunium stream for practical Purex process can not necessarily be success by the simple way proposed here, because the concentration of Np(VI), Np(V) and nitrous acid are varied with the condition of dissolution process. Further researches are required to simulate Np behavior in the Purex process precisely. The example, however, shows that the COMPAS is applicable to decide the operational conditions for the control of neptunium flow in the Purex process.

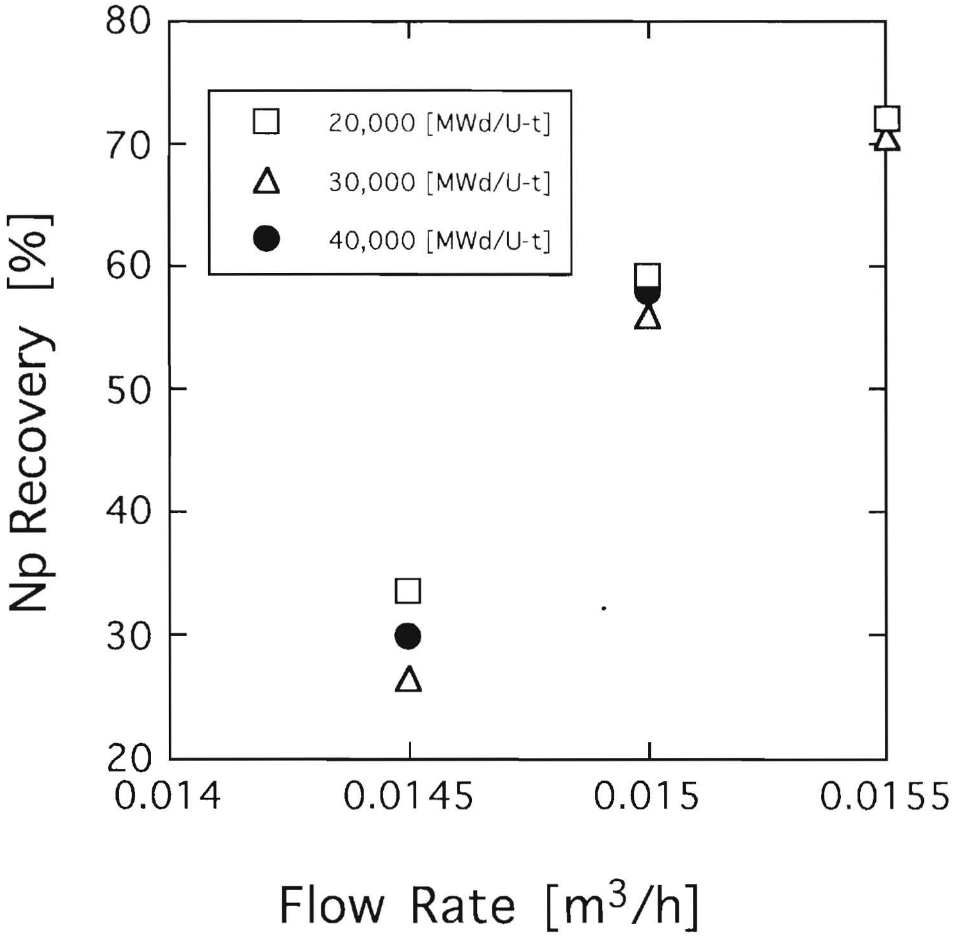

Fig.VI-2 Relationships between Np recovery and flow rate of the organic solvent

VI-4. Conclusion

The COMPAS has been developed in order to analyze the flowsheet of the Purex process. Drawing of a flowsheet diagram can be carried out easily by the mouse operation, therefore, the COMPAS copes with changes of the flowsheet. Results of the simulation are also obtained by the mouse operation and displayed graphically.

Determination of operational condition for control of neptunium flow was carried out as an application of the COMPAS. The results showed that the control of organic solvent feed rate to the co-decontamination process was one of available way to realize the control of neptunium flow in our example.

It is concluded that the COMPAS system is applicable to researches and engineering works in various parts of the fuel reprocessing.

References

1) Biegler, L.T.: "Chemical Process Simulation", *Chem.Eng.Prog.*, **85**[10], 50 (1989).

2) Harrison, J.W., Mills, A.L., Wilkins, M.: "REPROCX - A Reprocessing Flowsheet Computational System", *Proc.ISEC*'86, **1**, 131 (1986).

3) Homma, S., Sakamoto, S., Takanashi, M., Nammo, A., Satoh, Y., Soejima, T., Koga, J., Matsumoto S.: "Development of COMPAS, Computer Aided Process Flowsheet Design and Analysis System of Nuclear Fuel Reprocessing", *J.Nucl.Sci.Tecnol.* (in press).

4) Westerberg, A.W., Hutchison, H.P., Motard, R.L., Winter, P.: "Process flowsheeting", (1979), Cambridge Univ. Press.

5) Sakamoto, S., Homma, S., Koga, J., Matsumoto S.: "Process Flowsheet Design and Analysis System", *Sci.Eng.Reports Saitama Univ.*(in Japanese), **25**, 33 (1991).

6) Croff, A.G.: "A User's Manual for the ORIGEN2 Computer Code", *ORNL-TM*-7175, (1980).

CHAPTER VII

CONCLUSION

In this thesis, modeling of Purex process and its simulation were described. The major conclusions of the thesis are summarized as follows:

(1) The dissolution model of UO_2 pellets was suggested to simulate the dissolution process, which are controlled by both penetration and reaction. The reaction orders and rate constants in the model were determined from the experimental observations with the unirradiated oxide uranium fuel by the nonlinear least squares method. The rate equations presented here should be applicable to batch or continuous dissolver.

(2) The progression model was suggested to simulate the extraction behavior in the pulsed column. Simulation results by this model were in good agreement with the experimental ones. This model was also applicable to simulate the dynamic extraction behavior in the pulsed column. If the parameters of the progression model are represented as the operational conditions, the model will be more available.

(3) The new estimation equation of the distribution coefficient for Np(VI) was proposed. The estimation equations for the distribution coefficients of U(VI), Pu(IV) and nitric acid were also remade. These estimation equations have equilibrium constants which correlate with the total ionic strength in the aqueous phase. Distribution coefficients estimated by these equations are in good agreement with the presented distribution data.

(4) The qualitative analysis of the oxidation-reduction reaction between Np(V) and Np(VI) by nitrous acid was carried out and

the rate equation of the reaction was developed. The simulated concentration profiles of neptunium by the developed rate equation were fairly well agreement with experimental ones. A new approach building the simulation code was also suggested to easily extend the multi-component extraction system. All oxidation-reduction reactions in this model are assumed to occur only in aqueous phase. The approach in this study, which determines reaction rate equation from the extraction experiments, should be available for the analysis for the reaction kinetics of other components in the Purex extraction process.

(5) The COMPAS has been developed in order to analyze the flowsheet of the Purex process. Determination of operational condition for control of neptunium flow was carried out as an application of the COMPAS. The results showed that the control of organic solvent feed rate to the co-decontamination process was one of available way to realize the control of neptunium flow in our example.

These results should contribute the progress of the researches and developments of the Purex process, particularly in view of safety aspects and waste minimization.

NOTATION

a	Interfacial area	[cm^2/cm^3]
a	Fitting parameter;see Eq.(IV-11)	
b	Fitting parameter;see Eq.(IV-11)	
c	Fitting parameter;see Eq.(IV-11)	
d	Fitting parameter;see Eq.(IV-11)	
D	Distribution coefficient	[-]
H	Effective height of pulsed column	[cm]
K	Mass transfer coefficient in Chapter III	[cm/sec]
K	Equilibrium constant in Chapters IV and V	
K'	Apparent equilibrium constant	
k	Reaction rate constant	
k_p	Penetration rate constant;see Eq.(II-1)	[(l/mol)/min]
k_h	Reaction rate constant;see Eq.(II-2)	[$(l/mol)^2/min$]
k_n	Reaction rate constant;see Eq.(II-3)	[$(l/mol)^{(\beta+\chi)}/min$]
k_c	Reaction rate constant;see Eq.(II-4)	[$(l/mol)^3/min$]
m	Valence of actinide ion	
M	Molecular weight	
Q	Volumetric flow rate	[cm^3/s]
r	Reaction rate	
t	Time	[sec, min]
v	Volume of mixed tank	[cm^3]
V	Volume of column in Chapter III	[cm^3]
V	Reacting volume in Chapters II and V	[cm^3]
W_{ue}	Unexposed Mass of fuel or UO_2 pellet	[kg]
W_e	Exposed Mass of fuel or UO_2 pellet	[kg]
W_d	Dissolved Mass of fuel or UO_2 pellet	[kg]
x	Solute concentration in aqueous phase	[mol/cm^3, mol/l]
y	Solute concentration in organic phase	[mol/cm^3, mol/l]
y_x	Correlation coefficient of x;see Eqs.(IV-5)~(IV-8)	
z	Axial height of pulsed column	[cm]

Greek symbols

α	Reaction order;see Eqs.(II-2) and (IV-24)

β	Reaction order;see Eqs.(II-3) and (IV-24)	
χ	Reaction order;see Eq.(II-3)	
δ	Reaction order;see Eq.(II-4)	
ε	Reaction order;see Eq.(II-4)	
ϕ	Fractional holdup	[-]
μ	Ionic strength	[mol/l]

Subscripts

aq	Aqueous phase
d	Dispersed phase
eq	Equilibrium
i	Tank number
in	Inlet
init	Initial
j	Component
org	Organic phase
out	Outlet
x	Aqueous phase
y	Organic phase

Superscript

*	Equilibrium