



APPROACH TO THE EXTREME SAFETY IN A NUCLEAR FUEL REPROCESSING SYSTEM IN MILD AQUEOUS SOLUTIONS

N. Asanuma, Y. Asano, H. Tomiyasu, K. Mizumachi*,
Y. Ikeda**, M. Asou*** and M. Hanzawa****

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152; *: Meiji University, School of Science and Technology, Higashimita, Tama-ku, Kawasaki 214; **: Institute of Research Innovation, Kashiwa, Chiba 277; ***: Tokyo Electric Power Company, Nuclear Fuel Cycle Department, Egasaki-cho, Tsurumi-ku, Yokohama 230; ****: Mitsubishi Materials Corporation, Koishigawa, Bunkyo-ku, Tokyo 112.

ABSTRACT

The purpose of the present paper is to establish a new nuclear fuel reprocessing system, which is aimed to achieve the extreme safety. In order to avoid any potential danger of explosion, all processes are made by the precipitation method at room temperature. The system consists of the following processes: 1. crystallization of uranyl nitrate from a dissolved fuel solution by cooling the solution; 2. complex formation of UO_2^{2+} and Pu^{4+} with carbonate ion by the addition of Na_2CO_3 - NaHCO_3 solution adjusting pH to 9, followed by the separation of a precipitate containing the major fission products by the centrifugation method; 3. separation of Cs as a precipitate of cesium tetraphenylborate; 4. recovery of U and Pu as precipitates of hydroxo compounds from the alkaline solution by the addition of NaOH solution; 5. separation of Sr from the precipitate in process 2; 6. recovery of NaHCO_3 from the NaOH solution by bubbling CO_2 gas. As a result, 99.95% of the U was recovered with the least amount of fission products. Pu are expected to be recovered in the same way as U. In conclusion, the present reprocessing system enables us to recover U and Pu in high ratios from spent nuclear fuel by means of a simple precipitation method, to separate hazardous Cs and Sr from high-level waste, and to exclude any potential danger owing to chemical processes under mild aqueous conditions.

INTRODUCTION

In view of current nuclear fuel reprocessing, interest has been focused on the recoveries of U and TRU (transuranic elements) in high ratios because of their hazardous nature as long-life α -emitting radioactive elements. In order to reduce the toxicity of high-level waste, the separations of strong radioactive elements such as Cs and Sr are of particular importance as well. Among many subjects arisen in the nuclear fuel reprocessing, what is of primary importance is extreme safety and therefore any potential danger has to be avoided.

The PUREX is the only reprocessing method, which has been applied to commercial plants. Although this method is well designed and established to separate U and Pu from spent nuclear fuel, there still remain the following problems unsolved: dissolution of UO_2 fuel is made under severe conditions, i.e. in high concentration of HNO_3 at nearly boiling temperature; organic solvents used have potential danger of explosion and flammability; high recovery ratios

(more than 99.9%) for U and TRU have not been established yet, though recent extraction methods of recovering TRU using CMP (carbamoymethylphosphonate) and CMPO (carbamoymethylphosphine oxide) have been in progress [1]; the amount of non-radioactive waste produced by means of the extraction method is extremely large. Recently, the pyrometallurgical reprocessing method is in great progress [2]. As a matter of fact, this method appears to succeed to recover U from molten salts in high ratio. However, difficulty arises rather in the fundamental of this method how to keep the safety of the system under such severe conditions at temperature as high as 500°C containing exothermic and volatile radioactive elements such as Cs.

In the earlier reprocessing methods, the recovery of pure Pu was primary important and little attention was paid for the recovery of minor actinides [3]. For the purpose of nuclear fuel cycle, least amount of impurities are allowed in recovered U and TRU, while extremely high recovery ratios for these elements are required in order to reduce the toxicity of high-level waste. On the basis of these facts, we propose a new concept for the nuclear fuel reprocessing that sufficient amount of fission products should be removed from the spent nuclear fuel instead of separating U and Pu from fission products. This concept should result in the recoveries of U and Pu in high ratios.

EXPERIMENTAL

Experiments were carried out for a simulated spent fuel, which was calculated from the ORIGEN code for a PWR (pressurized water reactor) fuel (4.5% of initial ^{235}U enrichment, burn-up ratio 45,000 MW/D, specific power 38 MW/D and four years cooling). The species of U(VI) and 17 major fission products used as the simulated spent nuclear fuel are as follows: $\text{UO}_2(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Y}(\text{NO}_3)_3$, $\text{ZrO}(\text{NO}_3)_2$, $\text{Rh}(\text{NO}_3)_3$, $\text{Pd}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{La}(\text{NO}_3)_3$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\text{Pr}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$, $\text{Sm}(\text{NO}_3)_3$, CsNO_3 , RbNO_3 , H_6TeO_6 , Re_2O_7 , Na_2MoO_4 and $\text{RuNO}(\text{NO}_3)_3$. These species were dissolved in 1M HNO_3 solution. The concentration of the elements were determined by either ICP emission spectrophotometric (Perkin Elmer Optima 3000) or flame analysis (Hitach Z-5000) methods. The pH of the simulated fuel solution was adjusted to 9 by 0.5M Na_2CO_3 - NaHCO_3 solution. The precipitates were separated by filtration or centrifugation (2500rpm) using a Kubota model KS-4000.

For the separation of Cs, $\text{Na}(\text{C}_6\text{H}_5)_4\text{B}$ was used as a precipitant of Cs. Precipitation separation of Sr was made by using 18-crown-6 (MERCK KGaA) and silicotungstic acid 26 water (Kanto Chem. Co., Inc.). Unless otherwise stated, all chemicals used were reagent grade and were manufactured by Wako Pure Chem. Industries, Ltd. or Aldrich Chem. CO.. Water used was distilled after deionization.

RESULTS AND DISCUSSION

Scheme of the New Reprocessing System

The present reprocessing system is based on a new concept, where fission products are removed by the precipitation method from spent nuclear fuel keeping U and Pu in a solution. This concept is completely the reverse of the conventional methods, where U and Pu are separated from spent nuclear fuel. For extreme safety, all processes are made in aqueous solutions under mild conditions without using any flammable organic solvent. In order to decrease the radioactivity of radioactive waste, strong radioactive elements, such as Cs and Sr, should be separated. These separations would be better in the earlier stage of reprocessing system prior to the recovery of U and Pu. Experiments were carried out for the simulated spent nuclear fuel solution, which was calculated from ORIGEN code, containing U and 17 elements.

The present reprocessing system is shown in Fig. 1.

Crystallization of Uranyl Nitrate

By the uranyl nitrate crystallization method, U is partly removed from the dissolved fuel solution. The crystallization process has some advantages. The one is to decrease the concentration of uranyl ion in the dissolved fuel solution. As a matter of fact, about 70% of U was removed from 3M HNO₃ solution by the crystallization at -20°C [4]. In this case, the concentration of U in the dissolved fuel solution decrease from 1M to approximately 0.2M, under which condition the formation of actinyl carbonato complexes (following process) can be made more easily. The crystallization process enables us to control the proportion of U in the recovered actinide elements, since only uranyl ion crystallized from the dissolved solution. In order to avoid the mixing of Pu and Np into the crystallized uranyl, both NpO₂²⁺ and PuO₂²⁺ have to be reduced to NpO₂⁺ and Pu⁴⁺, respectively, by the addition of NaNO₂.

Complex Formation of U(VI) and Pu(IV) with Carbonate Ion

The addition of Na₂CO₃-NaHCO₃ solution results in the formation of carbonato complexes of hexa-valent actinyl ion, MO₂²⁺, i.e. [UO₂(CO₃)₃]⁴⁺, and Pu⁴⁺. Uranyl carbonato complexes are considerably soluble in basic solution. The solubility of U(VI) was nearly 0.2M at pH 7-9 [5]. Under such condition, most of the fission products were precipitated by forming either hydroxo compounds or insoluble carbonate salts. The results of the experiments with the simulated dissolved solution are listed in Table I. Alkaline earth elements, Sr and Ba, are precipitated over 90% as carbonate salts. Lanthanide ions are precipitated nearly 100% as hydroxo compounds. Similarly, Te, Y and Rh are precipitated in high ratios. On the other hand, Zr, Ru and Mo were only partly precipitated. Alkaline metals, Cs and Rb, and Re remained nearly 100% in the solution. Re was used to simulate the presence of Tc. The precipitation occurred instantaneously and the precipitate was completely separated by centrifugation from uranyl ion remained in the solution as carbonato complexes. The tri-valent actinide ions, Am(III) and Cm(III), behave similarly to tri-valent lanthanide ions and are expected to precipitate with them. The penta-valent Np is expected to precipitate as hydroxo compounds under such basic condition.

Separation of Cs

It is well known that sodium tetraphenylborate (Na(C₆H₅)₄B) is a specific precipitant of Cs [6]. An aqueous solution containing Na(C₆H₅)₄B was mixed with the simulated solution after removing the precipitate occurred by the addition of Na₂CO₃-NaHCO₃ solution. The precipitation ratio of Cs is nearly 100% (table II). The precipitates contain not only Cs but also Rb and Pd.

Recovery of U and Pu

Sufficient amount of fission products were removed from the dissolved fuel solution by adding Na₂CO₃-NaHCO₃ and Na(C₆H₅)₄B solutions. In the solution after removing Cs as the precipitate of tetraphenylborate salt, some elements still remain partly or fully with U(VI) ion, i.e. Mo remains ~60%, Zr ~20% and Ru ~30%, and Re remains nearly 100%. Considering the similarity of chemical behavior between Tc and Re, Tc is expected to remain fully in the solution. In order to recover U as hydroxo compounds, NaOH was added to this solution. As seen in Table III, the concentration of residual U in the solution was 4ppm, and accordingly the recovery ratio of U was 99.95%. Zr behaved similarly to U and thus Zr mixes into the precipitate. Mo precipitated only 8%. Tc is expected to remain in the solution, so that Re used instead of Tc remained fully in the solution. The result indicates that U can be well recovered as

precipitate from alkaline solution with impurities of only Mo and Zr. Note, however, that Mo and Zr are already partly removed in the earlier process and that these elements would not cause any serious problem if the recovered U becomes nuclear fuel without further purification. Pu is expected to recover as precipitates of hydroxo compounds like U.

Separation of Sr

In Fig. 1, the precipitate formed by the addition of $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ solution contains most of the fission products such as Sr and lanthanides as well as minor actinides, i.e. Np, Am and Cm. Unlike the actinide and lanthanide ions precipitated as hydroxo compounds, the alkaline earth ions precipitated as insoluble carbonate salts. These carbonate salts tend to be soluble in slightly acidic solutions. As a matter of fact, Sr and Ba salts are soluble at pH 6, under which condition the hydroxo compounds of lanthanide ions are still insoluble. Therefore, if the precipitate 1 in Fig. 1 is washed by slightly acidic solutions, Sr and Ba should be removed from the precipitate. Experiments were carried out as follows: the precipitate was dissolved again in 1M HNO_3 and then pH of the solution was varied by adding $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ solution. As seen in Fig. 2, over 95% of Sr remained in the solution with Ba, while other elements, lanthanides, noble metals, Zr and Mo, were precipitated in high ratios.

Another method for the separation of Sr is a precipitation method. It is well known that Sr ion forms complexes with crown ethers, especially with 18-crown-6. This complex forms insoluble compound with silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$) [7]. Experiments were carried out in both HNO_3 and HCl solutions. It was found that the precipitation ratio of Sr was 100% in 3M HCl, while 84% in 3M HNO_3 (Fig. 3).

Recovery of Na

In the present reprocessing system a large quantity of Na is used. Na accumulates in the alkaline solution after recovering U (solution 4 in Fig. 1). In order to decrease the amount of radioactive waste, Na is recovered from the alkaline solution as NaHCO_3 salts. Experiments were carried out by bubbling CO_2 gas through NaOH solution, followed by cooling the solution. By this method, as seen in Fig. 4, about 70% of Na can be recovered from 3M NaOH solution. Recovery of Na enables us to decrease of the amount of radioactive waste, because the recovered NaHCO_3 salts can be used again in the beginning of the present system.

CONCLUSION

In the present study, we propose a new reprocessing system which is kept under mild aqueous conditions without using any organic solvent. Therefore the extreme safety should be satisfied. The results can be summarized as follows: crystallization of uranyl nitrate from a dissolved fuel solution makes it possible to decrease the concentration of U prior to the formation of actinyl carbonato complexes; addition of $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ solution adjusting pH to 9 results in the precipitation of major fission products such as rare earths, noble metals and Sr as well as minor actinides, Np(V), Am(III) and Cm(III), which were separated from U(VI) and Pu(IV) forming high soluble carbonato complexes; separation of Cs was efficiently made by adding tetraphenylborate ion as a precipitant; Sr can be completely separated from the first precipitate by using 18C6 and silicotungstic acid; U was recovered in a high ratio as hydroxo compounds by the addition of NaOH and the same result is expected for Pu; Na was recovered from the NaOH solution by bubbling CO_2 gas and the recovered NaHCO_3 can be used again in the system. Sufficient amount of fission products remove from the spent nuclear fuel by the present reprocessing system. In Table IV, amounts of impurities in 1g recovered U are

summarized. Simulated fission products in 1g recovered U was in the order of 10^{-5} g or even less except for Zr and Mo. Since the crystallization method decreases the proportion of U compared to Pu, the finally recovered U and Pu can be used as a mixed-oxide fuel.

The new reprocessing system has been established by a simple precipitation method under mild aqueous condition without any potential danger, where the extreme safety should be guaranteed.

Acknowledgements

This paper has been partly supported by a Grant-in-Aid for Scientific Research (A)(2) No. 08409004 for the Ministry of Education, Science and Culture of Japan.

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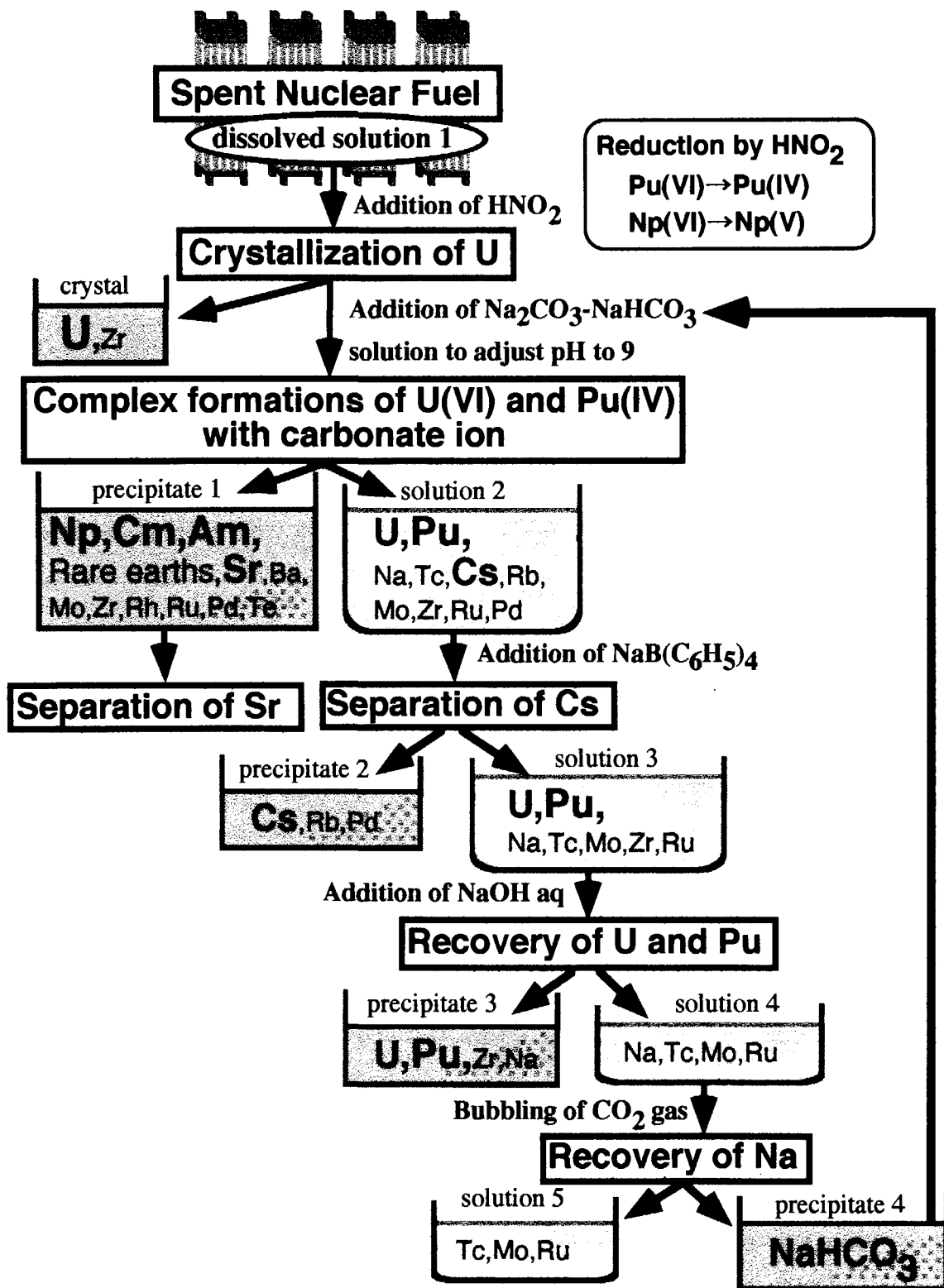


Fig.1 Schematic Diagram of The New Reprocessing System

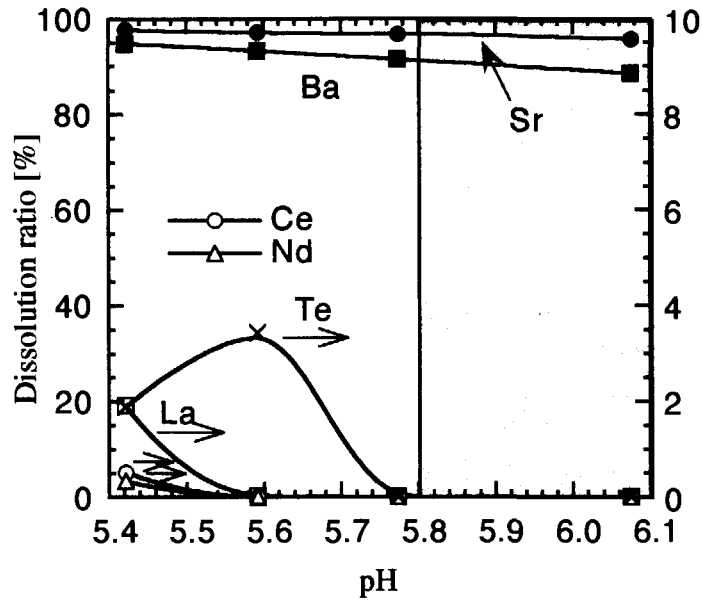


Fig. 2 Dissolution ratios of simulated fission products as a function of pH by adding $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ solution
 Rare earths, except for La, Ce and Nd, noble metals, Zr and Mo completely precipitated in this pH region.

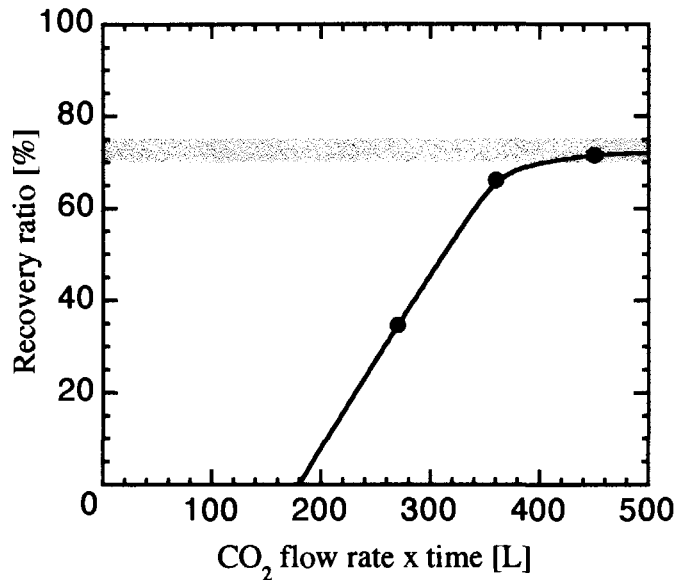
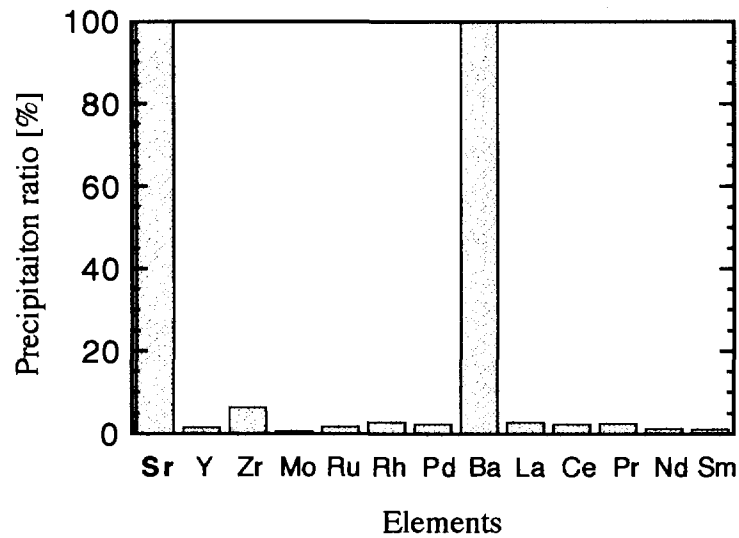
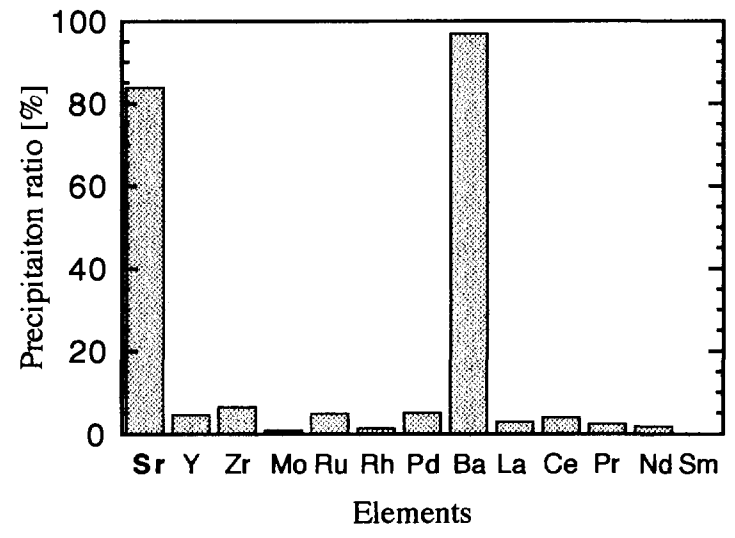


Fig. 4 Recovery ratio of Na in 3M NaOH solution
 CO_2 gas flow rate : 3.0 L/min, Temperature of the solution : $\sim 5^\circ\text{C}$
 — The maximum recovery ratio calculated from NaHCO_3 solubility at the given temperature



a) in 3M HCl



b) in 3M HNO₃

Fig. 3 Precipitation ratios of simulated fission products after adding 18C6 and $H_4SiW_{12}O_{40}$: (a) in 3M HCl and (b) in 3M HNO₃

Table I The initial concentrations of simulated fission products and their residual concentrations after the pH was adjusted to 9 by adding 0.5M Na₂CO₃-NaHCO₃ solution^a

	Elements	Conc. (initial) [10 ² ppm]	Conc. (pH9) [ppm]	Precipitation ratio [%]	Decontami- nation factor
Alkaline metals	Cs	9.6	450	4	1
	Rb	1.4	69	0	1
Alkaline earth metals	Sr	2.6	9	93	14
	Ba	5.3	7	97	37
Rare earths	Y	1.6	2	97	39
	La	4.0	<1	100	>195
	Ce(IV)	7.8	2	100	190
	Pr	3.9	<1	100	>190
	Nd	13.5	2	100	329
	Sm	2.5	1	100	122
Noble metals	Ru(III)	7.4	90	75	4
	Rh(III)	1.3	2	97	32
	Pd(II)	3.2	64	59	2
Others	Zr(IV)	11.5	135	76	4
	Mo(VI)	11.3	329	40	2
	Re(VII) ^b	2.6	119	6	1
	Te(VI)	1.4	3	97	23

a The 0.5M Na₂CO₃-NaHCO₃ solution was mixed with the simulated dissolved fuel solution in the volume ratio of 1:1.

b Rhenium was used to simulate the presence of Tc.

Table II The concentrations of residual Cs and other elements of simulated fission products in Na₂CO₃-NaHCO₃ solution after addition of sodium tetraphenylborate (STPB)^a

	Elements	Conc. (initial) [10 ² ppm]	Conc. (after addition of STPB) [ppm]	Precipitation ratio [%]	Decontami- nation factor
Alkaline metals	Cs	9.6	<1	100	>234
	Rb	1.4	<1	>97	>34
Noble metals	Ru	7.4	52	73	4
	Pd	3.2	<1	>99	>56
Others	Zr	11.5	58	79	5
	Mo	11.3	155	44	2
	Re ^b	2.6	60	5	1

a The 0.10M STPB aqueous solution was mixed with an equivalent volume of the simulated fuel solution after removing the precipitate occurred by the addition of Na₂CO₃-NaHCO₃ solution.

b Rhenium was used to simulate the presence of Tc.

Table III The precipitation ratios of simulated fission products in Na₂CO₃-NaHCO₃ solution with sodium tetraphenylborate and NaOH solutions added^a

Elements	Conc. (initial) [10 ² ppm]	Conc. (after addition of STPB) [ppm]	Conc. (after addition of NaOH) [ppm]	Precipitation ratio [%]	Decontamination factor
Actinide	U(VI)	2380	17630 ^b	4	2204
Noble metal ^c	Ru	7.4	15	4	2
Others ^c	Zr	11.5	20	<1	>10
	Mo	11.3	50	23	1
	Re ^d	2.6	19	10	1

- a 1M NaOH solution was mixed with an equivalent volume of the simulated fuel solution which most of the fission products was removed by adding Na₂CO₃-NaHCO₃ solution and STPB solution in the volume ratio of 1:5.75 and 1:1, respectively.
- b The concentration of U in the precipitates was determined with a proportional counter, and the precipitation of U was assumed to be negligible.
- c The concentrations were determined for the simulated dissolved fuel solution without U(VI) in order to avoid the measurement error caused by a large amount of U(VI).
- d Rhenium was used to simulate the presence of Tc.

Table IV The ratios of simulated fission products in 1g recovered uranium

Elements	Conc. (initial) [10 ² ppm]	Amount of impurity in 1g recovered uranium ^a [g]
Actinide	U(VI)	1
Alkaline metals	Cs	< 5.7 x 10 ⁻⁵
	Rb	< 5.7 x 10 ⁻⁵
Alkaline earth metals	Sr ^b	7.5 x 10 ⁻⁵
	Ba ^b	5.8 x 10 ⁻⁵
Rare earths	Y ^b	2.8 x 10 ⁻⁵
	La	< 2.8 x 10 ⁻⁵
	Ce(IV) ^b	2.8 x 10 ⁻⁵
	Pr	< 2.8 x 10 ⁻⁵
	Nd ^b	2.8 x 10 ⁻⁵
	Sm ^b	2.8 x 10 ⁻⁵
Noble metals	Ru(III) ^c	5.7 x 10 ⁻⁴
	Rh(III) ^b	2.8 x 10 ⁻⁵
	Pd(II)	< 5.7 x 10 ⁻⁵
Others	Zr(IV) ^c	1.1 x 10 ⁻³
	Mo(VI) ^c	2.3 x 10 ⁻⁴
	Re(VII) ^{c,d}	5.7 x 10 ⁻⁵
	Te(VI) ^b	2.8 x 10 ⁻⁵

- a The amount of recovered U was calculated from the concentration of U(VI) in the filtrate which was 4 ppm finally.
- b These elements that remained in the solutions after adding Na₂CO₃-NaHCO₃ solution were assumed to be finally recovered with U(VI).
- c This was calculated based on the results of Table III. Zirconium was assumed to precipitate completely by adding NaOH solution.
- d Rhenium was used to simulate the presence of Tc.