

Extraction of Thorium and Uranium from Monazite (Refining by Solvent Extraction)

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Abstract

This paper describes the economical process of production of thorium and uranium salts from crude thorium-uranium hydroxide derived from monazite by the solvent extraction. This process obtained as an experimental result consists of the following operations: (1) crude thorium-uranium cake is dissolved in nitric acid; (2) both thorium and uranium are extracted with tributyl phosphate from nitric acid solution, and refining thorium-uranium hydroxide is precipitated; (3) hydroxide cake is dissolved in hydrochloric acid and uranium alone is extracted with tributyl phosphate from hydrochloric acid solution; (4) uranium in stripping solution is precipitated as sodium uranate with caustic soda; (5) after thorium in raffinate being precipitated as carbonate, thorium carbonate is dissolved in nitric acid and converted into thorium nitrate crystal. This process has a characteristics that the extraction and the separation of thorium and uranium can be carried out with the same solvent only by the conversion of the kind of acid, and also it offers some advantages that the products by this method is superior in quality and more cheap in cost to those by the conventional oxalate-carbonate method. This process has been adopted in the industry of thorium and uranium as one of the refining processes of these metals since 1956, in Japan.

Introduction

In Japan, the refining technique of thorium salts from monazite have progressed with the increasing demand of thorium nitrate which is used in the gas-mantle industry. Several years ago, the production of thorium nitrate was carried out by the alkali carbonate-hydrogen-peroxide method from a crude thorium oxalate cake. For the last few years, the refining of thorium and uranium by a solvent extraction^{1,2)} or ion-exchange method³⁾ has been studied widely. It has been recognized that the industrial application of these methods has some advantages of the more purity and the more cost-down as compared with the products of the conventional process. Accordingly, in Japan the study of thorium salt production process from monazite has been directed to the development of these techniques. The purpose of this research described in this paper is to seek for the best condition of the process which produces thorium nitrate and sodium uranate from the crude thorium-uranium

hydroxide derived from monazite by the solvent extraction, and to establish a series of runs of the process.

The first step in the treatment of monazite is the decomposition of the mineral. For that purpose, two methods have been developed in Japanese industry. The first method consists of attacking the mineral with concentrated sulfuric acid, and this method has been adopted most widely. Many studies^{4,5)} of the separation process of thorium, uranium and rare earths from this acid solution have been developed and the author also has once described the sulfuric acid-pyrophosphate method⁶⁾ as a typical process. The second method⁷⁾ of the treatment consists of attacking the monazite with sodium hydroxide, and transforming the mineral into watersoluble trisodium phosphate and mixed hydroxides of the rare earth elements and of thorium. In this method, thorium and uranium can be separated almost completely from the rare earth elements by the selective precipitation of hydroxide.

In this paper the author restricts the content of this study to the production technique of commercial grade thorium nitrate and sodium uranate, starting from the crude thorium-uranium hydroxide obtained by the alkaline process or by the acid process of monazite decomposition, and refers the production process of the crude thorium-uranium hydroxide cake from monazite to the other literature. This study was done in Mar. 1956, and the outline of its contents was reported at the Annual Meeting of the Mineralogical Society of Japan on June 5, 1956.

Raw material

The chemical composition of the crude thorium-uranium hydroxide cakes obtained, on an industrial scale, by the alkaline and acid processes of monazite decomposition is shown in Table 1.

Table 1. Composition of crude thorium-uranium hydroxide.

monazite decomposition method		alkaline process			acid process		
no.		(1)	(2)	(3)	(1)	(2)	(3)
component							
ThO ₂		31.20	31.96	34.17	37.58	36.56	36.70
U ₃ O ₈		2.36	1.82	2.23	2.04	2.94	2.58
R ₂ O ₃		4.44	3.56	4.07	1.52	1.60	1.70
Fe ₂ O ₃		6.40	5.76	7.84	0.71	0.87	} 1.75
TiO ₂		5.52	7.32	8.64	0.69	0.47	
P ₂ O ₅		1.16	1.57	1.31	2.34	2.06	1.72
SiO ₂		7.36	7.99	4.47	1.41	1.67	1.56
H ₂ O [±]		40.23	38.63	36.20	53.29	53.49	53.43

[Treatment]

Alkaline process—a finely crushed monazite sand was treated with 37% caustic soda at 140°C for 2 hrs. The mixture was next immersed in hot water and filtered. After the cake

had been dissolved in conc hydrochloric acid, the acid solution was neutralized until pH 5.8 with dilute caustic soda solution. The recovery of the precipitate which has occurred was carried out by a series of thrice filtrations and twice washings.

Acid process⁶⁾—monazite sand was treated with conc sulfuric acid at 250°C for 2 hrs. The mixture was extracted with water. Uranyl in the solution was next reduced to uranous state by the immersion of aluminium and the dissolution of sodium hyposulfite. To it was added sodium pyrophosphate. Then, the precipitate was filtered and washed. After the pyrophosphate cake has been heated with caustic soda solution until 120°C. The mixture was immersed in hot water, filtered and washed.

Experiment and Discussion

(I) *Outline of method*

The process which has been developed as a result of the investigation involves the following operations:

- (i) dissolution of crude thorium-uranium hydroxide in nitric acid, and removal of insoluble material by filtration.
- (ii) extraction of thorium and uranium with tributyl phosphate, and precipitation of refined thorium-uranium hydroxide from stripping solution.
- (iii) dissolution of hydroxide in hydrochloric acid, and extraction of uranium with tributyl phosphate.
- (iv) precipitation of sodium uranate by the sodium carbonate-caustic soda method from stripping solution.
- (v) precipitation of pure thorium carbonate from raffinate and crystallization of thorium nitrate from its nitric acid solution.

This process was carried out first in the synthetic sample on a small scale and subsequently on a large scale (5 kg of ThO₂/1 lot) in pilot-plant equipment.

(II) *Laboratory study*

- (i) Extraction of thorium nitrate and uranyl nitrate with tributyl phosphate.

As a specific density of solvent, a metal distribution coefficient in solvent and a aqueous phase quantity into solvent are influenced by the kinds of diluent in tributyl phosphate, the selection of diluent is an important work which should be carried out before the experiment of solvent extraction. It has been recognized by the results of the examination⁸⁾ that when kerocen, benzen, toluen and carbon tetrachloride are used as diluent of TBP, the uranium metal distribution coefficients are increased according to the above arrangement of the diluents. But kerocen which has the most high boiling point and is more stable compound has been generally used as the diluent of TBP in a industrial process. Therefore, the author used kerocen in this process. For the TBP concentration in TBP—kerocen system of this process the author adopted 30 per cent in volume, which has been shown in several books.

The method of the extraction test is as follows; (1) both test solution and solvent are transferred into a separating funnel; (2) the funnel is immersed in thermo-hygrostat at 20°C for 30 minutes; (3) the funnel is next shaken for 3

minutes and settled for 10 minutes; (4) two phases of solvent and aqueous solution are separated; (5) a stripping process is carried out three times with water. The distribution coefficient and extraction ratio of thorium, uranium, acid etc., were calculated from their contents in raffinate and in stripping solution.

The each metal concentration in synthetic solution for solvent extraction was prepared in conformity with the composition of crude thorium-uranium concentrate (Table 1) and their concentration was adjusted to thorium, 100 g of ThO_2 , uranium, 10 g U_3O_8 , rare earth metals, 10~30 g R_2O_3 , iron, 10~20 g Fe_2O_3 and phosphorus 10~30 g P_2O_5 per litre as a standard.

The important factors which influence the extraction ratio and the purity of thorium nitrate and uranyl nitrate in a tributyl phosphate extraction are a concentration of salting out agent, a metal concentration in feed, a volume ratio of solvent to feed, an extraction temperature, a condition of stripping and back washing etc. The following experiments were carried out for the determination of the best condition of each of the above-mentioned factors.

(1) Effect of nitric acid concentration

When nitric acid was used as salting out agent, the distribution coefficients of thorium and uranium accompanying the variation of nitric acid concentration in feed were sought, and the best acid concentration for the extraction of these metals was decided from these distribution coefficients.

First, by means of shaking with 10 c.c. of 2~10 M-nitric acid and 10 c.c. of solvent, the amount of nitric acid transferred into solvent was determined, and next 10 c.c. of 2~6 M-nitric acid solution containing thorium, 100 g ThO_2/l and uranium, 10 g $\text{U}_3\text{O}_8/l$ severally, was extracted. These distribution coefficients calculated from the several above experiments are shown in Fig. 1.

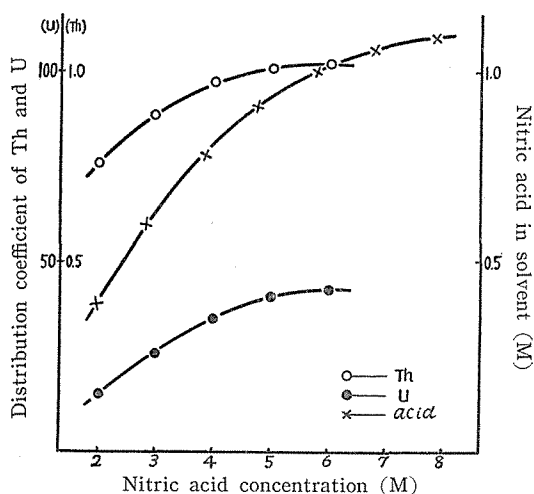


Fig. 1. Distribution coefficient of nitrate of Th and U and soluble quantity of HNO_3 in solvent at TBP extraction in nitric acid solution to various nitric acid concentration.

These distribution coefficients calculated from the several above experiments are shown in Fig. 1.

According to Fig. 1, it is recognized that the distribution coefficients of thorium and uranium increase with the increase of nitric acid concentration, and at the acid concentration of more than 4 M, the increase ratio of distribution coefficient per 1 M-nitric acid decreases and at 5~6 M, it shows almost a maximum value. At more than 4 M, the higher the acid concentration is, the smaller the gradient of nitric acid contents in solvent is. A following reason is presumed as an explanation of this fact. The

increase of nitric acid concentration in feed ensues the increase of undissociated $[\text{Th}(\text{NO}_3)_4]$ and $[\text{UO}_2(\text{NO}_3)_2]$ which form with TBP $\text{Th}(\text{NO}_3)_4 \cdot 4\text{TBP}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ by a common ion effect owing to the increase of $[\text{NO}_3]$, but the increase of nitric acid concentration in feed also causes consequently the increase of undissociated $[\text{HNO}_3]$ which forms $\text{HNO}_3 \cdot \text{TBP}$ with TBP. Therefore, TBP which should be combined with thorium and uranium is consumed by this reaction. As a result of the cancel of these opposite phenomena, the distribution coefficient of thorium and uranium becomes a maximum value at 6 M-nitric acid concentration in feed. Accordingly, it is desirable that nitric acid concentration in feed is adjusted to 6 M. However, it is desirable industrially to adopt 4 M for acid concentration in feed, considering the relation between nitric acid quantities used to raise the acid concentrate and extracted quantities of thorium and uranium.

(2) Effect of metal concentration in feed

In a batch solvent extraction, an extraction ratio of thorium and uranium is influenced by the concentration of these metals in feed. In order to determine this relationship, 10 c.c. of 4 M-nitric acid solution which contains the various quantities of thorium and uranium was extracted by TBP of an equal volume to the aqueous solution. These experimental results are shown in Table 2.

Table 2. Distribution coefficient and extraction ratio of nitrate of Th and U to variable metal concentration in feed.

uranium			thorium		
$\text{UO}_2(\text{NO}_3)_2$ in feed (U_3O_8 g/l)	distribution coefficient	extraction ratio (%)	$\text{Th}(\text{NO}_3)_4$ in feed (ThO_2 g/l)	distribution coefficient	extraction ratio (%)
10	29.7	96.73	50	1.95	66.10
30	24.1	96.02	62	1.60	61.54
50	21.2	95.50	75	1.35	57.45
80	13.8	93.24	100	0.98	49.50
100	8.35	89.30	150	0.75	42.86
150	3.05	75.31	200	0.60	37.50

As shown in Table 2, the extraction ratio and distribution coefficient of thorium and uranium decrease according to the increase of these metal contents in feed. The distribution coefficient of uranium shows the value rising one place in comparison with that of thorium, and the concentration of uranium, on the contrary, is usually one place lower than that of thorium. Accordingly, in this case it is not always necessary to consider the uranium concentration in feed, because it exists in constant proportion to the thorium concentration.

In an adoption of a batch extraction, it is not desirable industrially to lower the thorium concentration owing to the rise of production cost per unit, even if extraction ratio of it increases. The extraction ratio of thorium in the actual process is usually required more than 80%. It is determined from the value in Table 2

that the thorium concentration in feed, which is able to reach this value by a limited multiple extraction, is 100 g of ThO_2/l of feed, in maximum. This thorium concentration was adopted in the subsequent experiment.

(3) Effect of volume ratio of solvent to feed.

As the process of solvent extraction, there are two methods: one is a batch extraction, the other is a continuous extraction. The continuous extraction is fit for such material of relatively smaller distribution coefficient as thorium, but at the present when the demand of thorium is little, the batch extraction method is desirable for thorium extraction owing to the low price of equipment. Therefore, the batch extraction method was adopted in the following experiments. In the batch extraction, both the volume ratio of solvent to feed and the number of times of multiple extraction are the important factors which have much influence upon the extraction ratio of thorium and uranium. A volume ratio required to obtain the desirable metal extraction ratio was sought experimentally, and it can be calculated by the following formula.

$$\text{Forg./Faq.} = \frac{\rho}{D(1-\rho)} \quad \begin{array}{l} \rho = \text{extraction ratio} \\ D = \text{distribution coefficient} \end{array}$$

Fig. 2 shows the extraction ratio of each metal sought by means of shaking on 100 c.c. of 4M-nitric acid solution containing thorium, 100 g ThO_2/l , uranium 10 g $\text{U}_3\text{O}_8/l$ and rare earth metals, 10 g $\text{R}_2\text{O}_3/l$ respectively with TBP under the variable volume ratio of solvent to feed, 1.0, 1.5, 2.0 ... 3.5. From Fig. 2, it is found that the extraction ratio of thorium and uranium are nearly constant at volume ratio more than 3, but the extraction ratio of rare earths increases in proportion to the increase of the volume ratio.

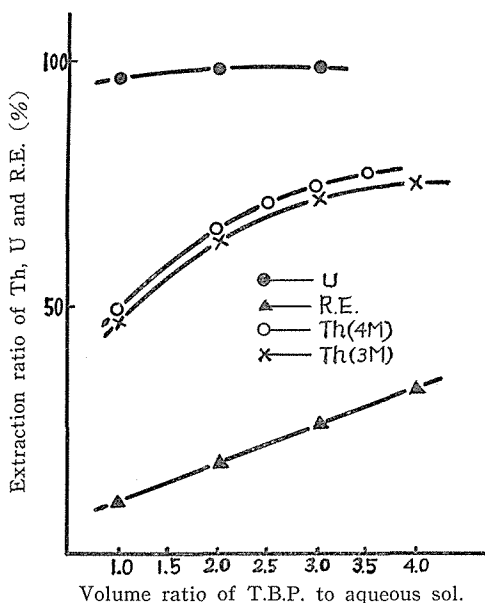


Fig. 2. Extraction ratio of nitrate of Th, U and R.E. to various volume ratio (solvent/feed) at TBP extraction in nitric acid solution.

The experiment seeking for the relation between the repeated times of extraction and the extraction ratio of thorium, uranium, etc., was carried out with 100 c.c. of 4M-nitric acid solution containing thorium (100 g ThO_2/l), uranium (10 g $\text{U}_3\text{O}_8/l$) and rare earths (10 g $\text{R}_2\text{O}_3/l$) together, with TBP, whose volume ratio to the solution is 2. Before 2nd and 3rd extraction, nitric acid was added for the adjustment of acid concentration in raffinate. This results is shown in Table 3.

Table 3. Extraction ratio of nitrate of Th, U and R.E. to the number of times of multiple extraction at TBP extraction.

a number of times of extraction		1st ext.		2nd ext.		3rd ext.		total	
kind of nitrate	acid (M)	weight (g)	ratio (%)	weight (g)	ratio (%)	weight (g)	ratio (%)	weight (g)	ratio (%)
thorium (ThO ₂)	3.0	6.403	64.03	2.053	20.53	0.534	5.34	8.990	89.90
" "	4.0	6.622	66.22	2.324	23.24	0.461	4.61	9.405	94.05
uranium (U ₃ O ₈)	4.0	0.9720	97.20	0.0230	2.30	0.0031	0.31	0.9981	99.81
rare earths (R ₂ O ₃)	4.0	0.0193	1.93	0.0185	1.85	0.0175	1.75	0.0553	5.53

From the results of Fig. 2 and Table 3, it is advisable that the volume ratio of TBP to feed is adopted in the range 2~3, on account of the facts that the thorium extraction ratio increases with the increase of volume ratio of TBP to feed, but the increase of thorium extraction ratio has the limit as above mentioned, and that the increase of impurity metal extraction ratio and the decrease of treatment amount of one lot occur accompanying the increase of volume ratio. Then, it is recognized that twice extractions with TBP, whose volume ratio to the solution is from 2 to 3, is at least required to secure the thorium extraction ratio, more than 80 per cent as above mentioned.

(4) Effect of impurity in crude thorium concentrate

The elements which are contained relatively much in crude thorium cake and influence the solvent extraction of thorium and uranium, are phosphorus, iron and rare earth elements. The presence of phosphorus impedes the solvent extraction of thorium and uranium, but this negative action of phosphorus is somewhat restrained by ferric iron in feed. A part of iron and rare earth metals is extracted by TBP and the purity of thorium and uranium extracted deteriorates in consequence of the admixture of these elements.

Phosphorus—the relation between thorium extraction ratio and phosphoric acid concentration in aqueous solution, was sought, using 50c.c. of 4M-nitric acid solution which contains both thorium, 100 g of ThO₂/l, and variable amounts of P₂O₅, by the twice extractions with TBP whose volume ratio to the solution is 2. These results are shown in Fig. 3.

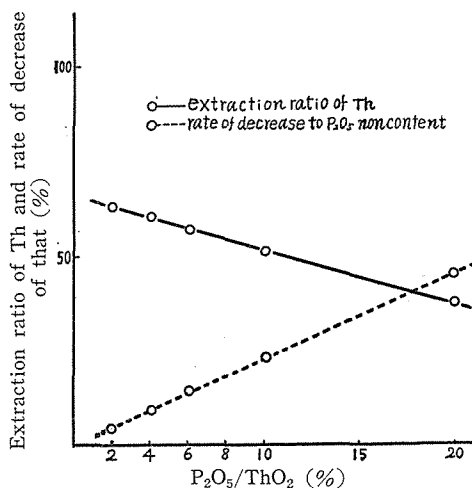


Fig. 3. Extraction ratio of thorium nitrate to various phosphorus concentration in feed at TBP extraction.

According to it, the thorium extraction ratio decreases in proportion to the increase of P_2O_5/ThO_2 and it is shown that the thorium extraction ratio when thorium contains P_2O_5 , P_2O_5/ThO_2 4% decreases 10% of that when it does not contain P_2O_5 ; when thorium contains P_2O_5 , P_2O_5/ThO_2 20% it decrease 50% of the later ratio. The contamination of P_2O_5 in this range is generally seen in the crude thorium-uranium hydroxide cake. Though this effect can be minimized by ferric nitrate in feed, the crude thorium hydroxide for solvent extraction should be kept low in phosphorus content.

Iron and rare earth elements—on 100 c.c. of 3M-nitric acid solution containing the variable quantities of iron and rare earth elements respectively, the extraction quantities of these metals were sought with 300 c.c. of TBP by twice extractions. These results are shown in Table 4.

Table 4. Extraction quantities of nitrates of Fe and R.E. to variable metal concentrations in feed at TBP extraction.

rare earth elements				iron			
in 100 c.c. feed, R_2O_3 (g)	extracted R_2O_3			in 100 c.c. feed, Fe_2O_3 (g)	extracted Fe_2O_3		
	1st (g)	2nd (g)	total (g)		1st (g)	2nd (g)	total (g)
1.000	0.0247	0.0277	0.0524	0.500	0.0126	0.0112	0.0238
2.000	0.0521	0.0444	0.0965	1.000	0.0194	0.0168	0.0362
3.000	0.1014	0.1192	0.2206	2.000	0.0311	0.0291	0.0602
5.000	0.2289	0.2428	0.4717	4.000	0.0611	0.0460	0.1071

Iron content in feed is variable in the above range according to localities of monazite sand and rare earths content is also variable by the separating technique of thorium at crude thorium-uranium hydroxide production. Since the more quantities of iron and rare earths in feed increase, the more extracted quantities of these metals increase, it is desirable to reduce the quantities of iron and rare earths in crude hydroxide to as little ones as possible, even these elements can be removed by means of back-washing, fractional precipitation or following solvent extraction.

(5) Stripping condition

Stripping process of TBP phase which recovers thorium and uranium was carried out with water. An effect of stripping on batch extraction process is influenced both by the number of times of stripping and by a volume ratio of water to TBP. After 100 c.c. of 4M-nitric acid solution containing 10 g of ThO_2 , 1 g of U_3O_8 , 2 g of R_2O_3 and 2 g of Fe_2O_3 respectively had been extracted with 300 c.c. of TBP, the solvent was stripped three times with 300 c.c. of water apiece. The result of their metal stripping ratio at each time is shown in Fig. 4. According to Fig. 4, by once stripping, more than 80% of thorium, rare earths and iron is stripped but nearly complete recovery of uranium at least requires thrice strippings.

The stripping facility of each metal has the inverse relation to the magnitude of distribution coefficient.

In order to seek the best industrial condition of stripping, after the extraction had been carried out by the above mentioned process with the solution containing thorium (100g ThO_2/l) and uranium (10 g $\text{U}_3\text{O}_8/l$) together, the stripped metal quantities were sought by treating with the variable volume of stripping water at each stripping. This results are shown in Table 5.

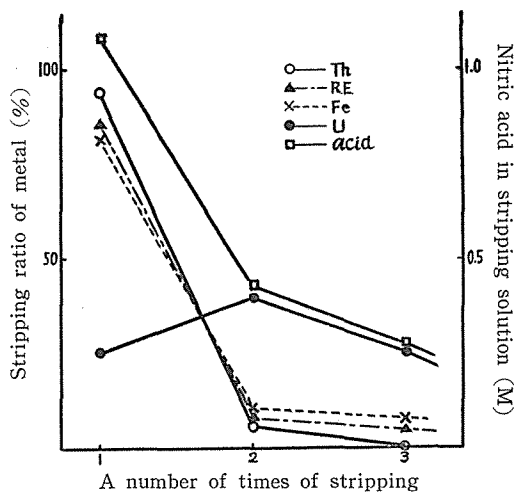


Fig. 4. Stripping ratio of nitrate of Th, U, Fe and R.E., to a number of times of stripping at TBP extraction.

Table 5. Stripping ratio of nitrate of Th and U to variable volumes of stripping water.

test no.	volume ratio of water to TBP		stripped metal			
	1st	2nd	thorium (ThO_2)		uranium (U_3O_8)	
			(g)	(%)	(g)	(%)
1	1	0	6.096	80.6	0.195	20.0
2	2	0	7.206	95.3	0.454	46.3
3	1	1	7.545	99.8	0.676	69.0
4	1	2	7.532	99.6	0.849	86.7
5	2	1	7.534	99.7	0.862	88.0
6	2	2	7.554	99.9	0.920	93.9

thorium content (ThO_2 7.560 g) and uranium content (U_3O_8 0.980 g) in solvent.

Although the sufficient stripping of thorium and uranium, especially of uranium is obtained with large volume of water and by twice strippings as at test 6, the remarkable increase of the extracted volume is undesirable from the industrial standpoint. In an industrial stripping process, a satisfactory result is obtained by carrying out with water, water/TBP. 2, at 1st stripping and water/TBP. 1, at 2nd. Although the stripping of uranium is not sufficient, the loss of uranium can be disregarded since unstripped uranium in TBP is transferred to the next lot extraction as the result of the recycle of TBP.

(6) Recovery of thorium and uranium as hydroxide from extracted solution

In this study, thorium and uranium in extracted solution were precipitated as hydroxide with ammonia for the purpose of the remove of nitrate ion which interferes with the succeeding TBP extraction in hydrochloric acid solution. By raising the pH of the solution to 6.0 ± 0.2 , more than 99% of thorium and uranium is precipitated but the reduced rare earths do not yet begin theoretically the precipitation at this pH. Accordingly, the rare earths which are extracted with thorium and uranium by solvent can be separated from thorium and uranium by the fractional precipitation. The small amount of rare earths, however, remains in the thorium-uranium hydroxide by the absorption reaction.

(ii) Separation of uranyl chloride and thorium chloride by tributyl phosphate extraction

For the separation method of thorium and uranium, an oxalic acid method⁹⁾ which separates thorium as precipitate from uranium solution with oxalic acid, and an ion-exchange method³⁾ which applies the difference of absorption capacity of these carbonate complex ions to anion resin, have been carried out and reported. Though the former method has been adopted widely since the development of thorium industry, this is not a best industrial method for the production of thorium nitrate, because it requires many operations to change the thorium oxalate into its hydroxide. The latter method is studied on a laboratory scale of late and not yet adopted for an industrial process. The author investigated the method by which uranium alone is extracted into TBP and thorium is left in raffinate by the TBP extraction in the hydrochloric acid solution in accordance with the discovery that thorium chloride remarkably differs from uranium chloride in their distribution coefficient in TBP. Distribution coefficient and separation coefficient of thorium and uranium were sought from the experimental result that thorium (100 g ThO_2/l) and uranium (100 g $\text{U}_3\text{O}_8/l$) in 4M-hydrochloric acid solution were extracted with 30% TBP by the process of solvent extraction as mentioned in section (i). These results are shown in Table 6. The distribution coefficient of the each metal nitrate was also described in Table 6 together with the purpose of comparison.

Table 6. Distribution coefficient and separation coefficient of chlorides of Th and U, and of nitrates of these metals at TBP extraction.

kind of salt	concentrate (g/l)	distribution coefficient	separation coefficient (U to Th)
uranyl chloride	U_3O_8 100	0.91	} 82.7
thorium chloride	ThO_2 100	0.011	
uranyl chloride	U_3O_8 10	6.13	} 557.2
uranyl nitrate	U_3O_8 100	7.62	
thorium nitrate	ThO_2 100	0.98	} 7.8
uranyl nitrate	U_3O_8 10	36.00	

From the values of the distribution coefficient of thorium and uranium, it is found that uranium in hydrochloric acid is well extracted with TBP, but thorium is not almost extracted. In the following experiments, the separation conditions of uranium and thorium in hydrochloric acid solution were determined.

(1) Effect of hydrochloric acid concentration

The results are shown in Fig. 5, that the relation between the quantities of hydrochloric acid transferred into TBP and hydrochloric acid concentration in feed was determined with 10 c.c. of 2~10M-hydrochloric acid, and that the distribution coefficient of uranyl chloride and of thorium chloride at each acid concentration was determined with 10 c.c. of 2~6M-hydrochloric acid solution containing uranium (10g U_3O_8/l), and thorium (100g ThO_2/l). According to Fig. 5, the quantities of the hydrochloric acid transferred into TBP increase abruptly at 5M-acid concentration in feed, and the distribution coefficients of uranium and thorium also increase as well as acid quantity in TBP.

The facts that the distribution coefficients of uranium chloride and thorium chloride show the large difference, and that the soluble quantity of hydrochloric acid in TBP exceedingly differs from that of nitric acid, are considered to occur perhaps by the difference of chloride and nitrate in the ionization degree. Further theoretical discussion on this problem, however, is not attempted in this paper.

The suitable hydrochloric acid concentration at which uranium is transferred into TBP and thorium remains in aqueous solution is 4~4.5M. Below 3M-hydrochloric acid, the solution is frequently emulsified in the actual process.

For the next experiment, 100 c.c. of solution that contains both thorium (100g ThO_2/l) and uranium (10g U_3O_8/l) and that contains also varied hydrochloric acid was treated with 200 c.c. of TBP. These results are shown in Table 7.

From Table 7, it is found that at the acidity 4.5M the extraction ratio of uranium and of thorium and the separation ratio of these metals reach 90%, 1.6% and 56%, and that at more than 4.5M the extraction ratio of uranium increases, while the separation ratio of uranium and thorium decreases. Accordingly, 4.5M-hydrochloric acid is the most suitable acid concentration in this process.

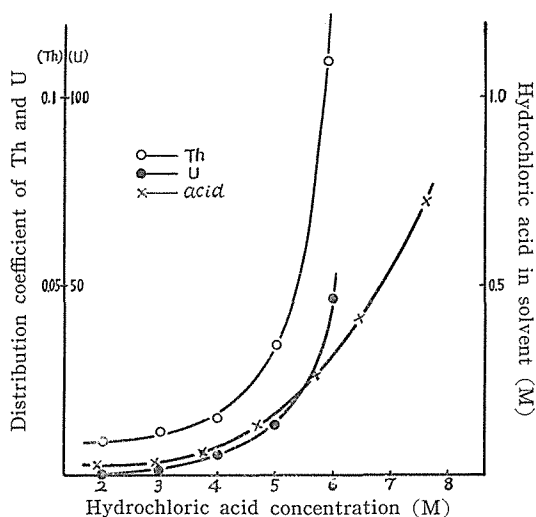


Fig. 5. Distribution coefficient of chloride of Th and U and soluble quantity of HCl in solvent at TBP extraction in hydrochloric acid solution to various hydrochloric acid concentrations.

Table 7. Extraction ratio of chloride of Th and U to varied hydrochloric acid concent.

acid (M)	extracted (ThO ₂)		extracted U ₃ O ₈	
	(g)	(%)	(g)	(%)
3.0	0.1132	1.13 (1.57)	0.7084	70.84 (66.7)
4.0	0.1490	1.49 (1.77)	0.8650	86.50 (92.4)
4.5	0.1596	1.60 (2.15)	0.8953	89.53 (95.0)
5.0	0.2964	2.96 (6.45)	0.9204	92.04 (96.3)
5.5	0.5260	5.26 (—)	0.9311	93.11 (—)
6.0	1.0944	10.94 (20.00)	0.9352	93.52 (96.9)

() the value in the case containing uranium and thorium separately

(2) Effect of volume ratio of TBP to aqueous solution

In order to determine the relation between the extraction ratio of uranium and thorium and the volume ratio of TBP to aqueous solution, with 100 c.c. of 4.5M-hydrochloric acid solution containing uranium (10g U₃O₈/l), and thorium (100g ThO₂/l), several experiments were repeated under the volume ratio of TBP to feed, 1.0, 1.5, ... 2.5. The result is shown in Fig. 6. According to Fig. 6, the volume ratio of TBP to aqueous solution, when it is 2, is thought fit to obtain the uranium

extraction ratio 90% and the separation ratio 56. At more than this volume ratio, the separation ratio decreases with the increase of the thorium extract.

(3) Effect of metal concentration in aqueous solution

The concentration of thorium, uranium, iron, rare earth metals etc. in hydrochloric acid solution is determined by the water content in hydroxide cake separated from the above nitric acid solution. When the undried cake filtered from the nitric acid solution was dissolved in 37% hydrochloric acid and its acid concentration was adjusted to 4.5M, the each metal concentration in the solution is, thorium, about 100g of ThO₂ per litre, uranium, about 10g of U₃O₈ per litre and iron, 0.1~0.5g of Fe₂O₃ per litre.

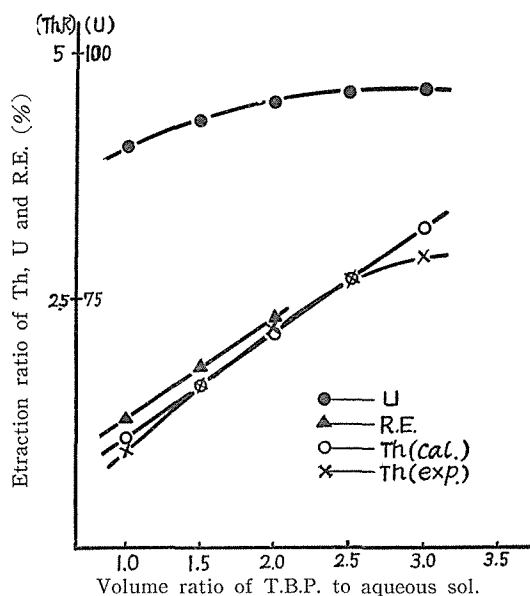


Fig. 6. Extraction ratio of chloride of Th, U and R.E. to varied volume ratio, (solvent/feed) at TBP extraction in hydrochloric acid solution.

With 4M-hydrochloric acid solution which contained more than the above quantities of iron and uranium, twice extractions were carried out with TBP, whose volume ratio to aqueous solution is 2; the experimental results are shown in Table 8.

Table 8. Extraction ratio of chloride of U, Fe, Th and R.E. to a number of times of multiple extraction at TBP extraction.

kind of chloride content in feed 100 c.c. (g)	uranium (U ₃ O ₈)			iron (Fe ₂ O ₃)			thorium (ThO ₂)	rare earths (R ₂ O ₃)
	1.0000	2.5000	5.0000	0.0500	0.1000	0.1500	10.000	1.0000
1st ext. quantity (g)	0.9521	2.2269	3.9865	0.0496	0.0986	0.1486	0.2188	0.0242
" ratio (%)	95.21	89.08	79.76	97.2	98.6	99.1	2.19	2.42
2nd ext. quantity (g)	0.0376	0.2362	0.9414	0.0012	0.0012	0.0011	0.2237	0.0189
" ratio (%)	3.76	9.44	18.83	2.4	1.2	0.7	2.24	1.89
total ext. ratio (%)	98.97	98.52	98.59	99.6	99.8	99.8	4.43	4.31

By Table 8, it is found that extraction ratio of uranium and iron is reached more than 95% by once extraction in the solution of thorium concentration, 100g ThO₂/l, but when uranium concentration is more than that, twice extractions are required. Rare earth elements also are partly extracted and this extraction process is useful to reduce the rare earths which can not be removed completely by both the TBP extraction of nitrate and the fractional precipitation of hydroxide.

(4) Stripping condition

The stripping of uranium from TBP treated in hydrochloric acid solution is more easy than the uranium stripping from TBP in nitric acid, because the uranium distribution coefficient in hydrochloric acid is smaller than that in nitric acid. The acid concentration in the stripping solution decreases speedily due to the fact that the quantity of hydrochloric acid transferred into TBP is little. In order to decide the amount of stripping, after 100 c.c. of 4M-hydrochloric acid solution containing thorium, uranium and iron respectively had been extracted with 300 c.c. of TBP, stripping process was carried out thrice with water, 300 c.c. at each stripping, and these metals in each stripping solution were analysed. The result is shown in Table 9.

Table 9. Stripping quantity of chloride of U, Fe and Th to the multiple times of stripping at TBP extraction.

kind of chloride content in feed 100 c.c. (g)	uranium		iron		thorium	
	0.1000 (U ₃ O ₈)		0.1000 (Fe ₂ O ₃)		10.0000 (ThO ₂)	
	(g)	(%)	(g)	(%)	(g)	(%)
once strip.	0.9388	98.60	0.0948	96.15	0.2158	99.56
twice strip.	0.0085	0.90	0.0027	2.74	0.0036	0.12
thrice strip.	0.0048	0.50	0.0011	1.11	0.0004	0.02
total	0.9521	100.00	0.0986	100.00	0.2188	100.00

1 hr. in order to evaporate nitrogen monoxide gas, which breaks down TBP. The acid solution in which was suspended solid material consisting mostly of silica, titania and iron oxide was filtered under a pressure with steel filter consisting of one horizontal plate. The slurry is washed with 70~100/ of water of the filter. The acid solution was then transferred into a storage tank. By this treatment, the concentration of acid and thorium in the solution was adjusted to 4~4.5M-nitric acid and to 95~110g of ThO_2 per litre. Concentration of a typical acid solution is shown in Table 10.

Table 10. Composition of nitric acid solution of crude hydroxide cake (feed for TBP extraction).

constituent	ThO_2	U_3O_8	R_2O_3	Fe_2O_3	TiO_2	P_2O_5	acid concentration (M)
grams per litre	99.82	8.21	4.34	2.39	0.87	2.80	4.1

(ii) Extraction of thorium and uranium with trybutyl phosphate and precipitation of hydroxide with ammonia

The extraction process of one batch consisted of twice extractions and twice strippings after each extraction. 50/ of feed of one lot was placed in mixer settler extractor (Fig. 8 A). Into it was charged 30% TBP-kerosene, 100/ of solvent/50/ of feed. After agitation for 10 minutes the mixture was settled for 30 minutes in order to separate two phases completely. The solvent phase transferred into the extractor (B) with syphon was stripped with water, 200/ of water/100/ of solvent, by agitating for 10 minutes. The mixture was settled for 30 minutes. The solvent was again transferred into the extractor (C) and twice strippings were carried out with water, 100/ of solvent. The solvent which had been twice stripped recycled to the first extraction of the next lot. The acid concentration of the raffinate obtained from the first extraction was adjusted to about 4M. by the addition of 14N nitric acid, 5kg of acid/50/ of feed. The second extraction and stripping were carried out in the above-mentioned process with fresh TBP (in the case of the next lot, with TBP which recycled from the second extraction of the preceding lot). Solvent which had been twice stripped at the second extraction recycled to the second extraction at the next lot extraction. Raffinate obtained from the second extraction was offered for the recovery of rare earths and unextracted thorium. Stripping solution from the first extraction and

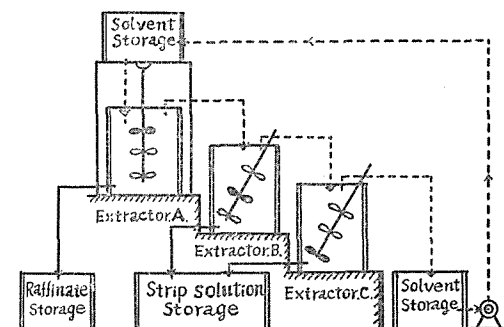


Fig. 8. Equipments of solvent extraction.

that from the second were combined in a neutralization vessel.

The combined solution was partially neutralized by the addition of ammonium hydroxide. This operation was carried out with a high speed agitation. Before neutralization, sodium nitride, 100 g of salt/50 l of feed, was added in order to reduce ceric salt. To the acid solution was added a dilute ammonium hydroxide until an equilibrium pH of 5.8~6.0 as measured with a glass calomel electrode pH meter. The separation of hydroxide slurry was required to carry out at least twice filtrations and one washing in order to remove the mother water containing nitrate and rare earths. Before each filtration, the slurry was settled and as much supernatant liquor as possible was removed by decantation. The filtrations were carried out with an rotary drum vacuum filter at 380 mm of Hg vacuum. After filtration, the cake was repulped and vigorously stirred in water. The repulped slurry was settled again, decanted and filtered. The final wet cake was transferred into a storage vessel. A typical analysis of obtained cake is given in Table 11.

Table 11. Yield and composition of refining thorium--uranium hydroxide cake.

comp.	ThO ₂	R ₂ O ₃	U ₃ O ₈	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	ig. loss	H ₂ O
(%)	16.55	0.025	1.39	0.018	0.001	0.032	2.07	79.93

Yield—Cake 24.5 kg. ThO₂, 4.05 kg (81.3%), U₃O₈ 0.34 kg (83.9%), () contents of Th and of U in thorium—uranium cake to these contents in feed.

(iii) Dissolution of hydroxide cake in hydrochloric acid and extraction of uranium by tributyl phosphate.

Thorium—uranium hydroxide cake was next transferred into stoneware vessel fitted with a steam-jacketed pfaudler. To it was added 35% hydrochloric acid, 20 kg of acid/50 kg of cake. The mixture was heated nearly to the boiling point for 30 minutes. By the heating, chlorine gas could be almost evolved from acid solution. The acid solution was then charged in a mixer settler extractor (Fig. 8). To it was added 30% TBP-kerosene, 100 l of solvent/50 l of feed. After mixing with moderate agitation for 10 minutes, the mixture was settled for 30 minutes in order to separate each phase of solvent and raffinate completely. The decomposed material of solvent often occurred between solvent and raffinate. Accordingly, the separation of the three phases of solvent, raffinate and decomposed material was required. The solvent and raffinate were separated from each other by syphon and transferred into the extractor (B) and a storage vessel. After the middle phase which consists mainly of decomposed material of solvent, had been filtered with a glass fiber filter, solvent and raffinate obtained by filtration were added to each main phase. The solvent was stripped with water, 200 l of water/100 l of solvent, by agitation for 10 minutes and settlement for 30 minutes. After the solvent had been separated by syphon, it recycled to solvent extraction of the next lot.

The stripping solution containing uranium was neutralized until pH 6.0 with 10% sodium carbonate-sodium bicarbonate solution (weight ratio of carbonate to bicarbonate is 1) with agitation. The supernatant liquor was transferred into a reaction vessel fitted with a steam-jacketed pfaudler. The precipitate which consisted mainly of iron and thorium was filtered in centrifugal filter, and its cake was repulped with water and again filtered. The final cake was used for the preparation of nitric acid feed with crude thorium-uranium hydroxide cake. Two filtrates were combined with the supernatant liquor. To it was added 35% hydrochloric acid until about pH 3 and the solution was heated to the boiling point in order to break carbonate complex and to remove carbon dioxide. After the heating had been finished, to it was added 10% sodium hydroxide solution until about pH 9 and the occurred uranium precipitate was settled, decanted and filtered. The cake was repulped in water, decanted and again filtered. The final wet cake was dried on oven at 100~110°C to constant weight. Composition and yield of the obtained yellow cake are given in Table 12.

Table 12. Yield and composition of natrium uranate cake (of the first lot).

comp.	U ₃ O ₈	Na ₂ O	ThO ₂ (R ₂ O ₃)	Fe ₂ O ₃	TiO ₂	Al ₂ O ₃	P ₂ O ₅	SiO ₂	ig. loss	H ₂ O
(%)	83.91	9.77	0.19	0.05	tr	tr	0.05	0.10	3.96	0.45

Yield—Cake 0.38 kg, U₃O₈ 0.32 kg, U in yellow cake to that in original feed, 78.0%.

(iv) Recovery of thorium salts

Raffinate containing thorium was diluted with water until three times as great volume as the raffinate. To it was added 10% ammonium hydroxide until thorium hydroxide began to precipitate (until about pH 2) and the addition of 5% ammonium bicarbonate solution was continued until pH 6.5. After the precipitate of carbonate had been settled completely, the supernatant liquor was removed by the help of pump. The slurry was repulped in water, settled and again decanted to remove as much chloride and remaining solvent as possible. The slurry filtered with a rotary drum vacuum filter. The cake was repulped in water, settled, decanted and again filtered.

The final cake was transferred into the reaction vessel fitted with a heater and dissolved in nitric acid until the clear solution is obtained by heating. The nitric acid solution was filtered with a suction filter in order to remove the fine segregated silica from the solution. The filtered acid solution was next evaporated in crystallizing dish until the surface of the solution was crystallized a little. By cooling with agitation of the solution, thorium nitrate crystal was segregated out with the evaporation of nitric acid gas. Composition of the obtained thorium nitrate is shown in Table 13.

Table 13. Yield and composition of obtained thorium nitrate crystal (of the first lot).

comp.	ThO ₂	R ₂ O ₃	Fe ₂ O ₃	TiO ₂	Al ₂ O ₃	CaO	U ₃ O ₈	SO ₄	P ₂ O ₅	SiO ₂	ig. loss	H ₂ O
(%)	47.75	0.05	0.01	0.02	tr	0.02	0.01	0.23	0.11	tr	47.80	3.84

Yield—Cake 8.30 kg, ThO₂ 3.96 kg, Th in thorium nitrate to that of original feed, 79.4%.

The obtained thorium nitrate can be supplied intact as commercial product, and for the purpose of the use of the atomic energy it should be purified by a solvent extraction or an ion-exchange process.

Conclusion

The process which has been investigated by the author, consists of following two main reactions:

- (1) Both thorium and uranium are extracted with tributyl phosphate from the nitric acid solution of the crude thorium-uranium hydroxide,
- (2) Uranium is extracted with tributyl phosphate from the hydrochloric acid solution of the refined thorium-uranium hydroxide and thorium remains in raffinate.

By applying these two reactions, the author succeeded in producing uranium yellow cake and commercial grade thorium nitrate from crude thorium-uranium hydroxide cake obtained from monazite by sulfuric acid treatment or caustic soda treatment.

The characteristics of this process is that the extraction and separation of thorium and uranium can be carried out with same solvent only by changing the kind of acid.

An industrial value of this investigation consists in that this process offers some advantages that the thorium and uranium products obtained are relatively purer, and their cost is down lower than those by conventional carbonate-hydrogen peroxide method of oxalate. Accordingly, this process has been used as one of the processes of the thorium and uranium production in Japan since 1956. Batch extraction in this process should be converted to continuous extraction with the increase of thorium demand, and the application of continuous extraction probably can be cost-down by the increase of extraction ratio and the improvement of working efficiency.

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