

Extraction of Uranium from Monazite

By

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Abstract

Monazite contains from 0.2 to 0.6 per cent of uranium as a minor element besides rare earths and thorium. This paper describes on the economical processes of recovering uranium in the process of rare earths production from monazite. This process consists of the following step by step operations: (1) Monazite sand is treated with sulfuric acid. (2) Uranium (VI) in the extracted solution is reduced to uranium (IV) with aluminium and hydrosulfite. (3) Uranium is precipitated as pyrophosphate being accompanied by thorium with sodium pyrophosphate. (4) The pyrophosphate (uranium (IV) and thorium) is converted into hydrous oxide with caustic soda solution, and then uranium (IV) in hydrous oxide is oxidized into uranium (VI) with sodium hypochlorite. (5) After hydrous oxide is dissolved in hydrochloric acid, the separation of uranium from thorium is carried out with oxalic acid. (6) Uranium (VI) in the filtrate is then separated as uranium (IV) oxalate by reducing uranium (VI) with metallic aluminium. (7) The uranium oxalate is converted into uranium oxide by burning. This process was appreciated as one of the most excellent by-product methods of uranium from the experimental and practical results and was adopted in the initial uranium industry in Japan.

Introduction

In Japan, Monazite sand is imported from Korea and South-east Asia, especially Malay and Thailand. The various rare earth compounds and metals are produced from this ore. Monazite is orthophosphate of thorium and rare earth which consists mainly of cerium group elements. In monazite sand, uranium is without exception contained from 0.2 per cent to 0.6 per cent.

The purpose of this study is to settle an extracting method of uranium in the process of rare earth production from monazite. For the treatment of monazite sand, there have been two methods; one is the sulfuric acid treatment which has been widely practised during the last quarter of this century, another is the caustic soda treatment¹⁾ which has developed since the beginning of the Atomic Energy Age. Though the caustic soda treatment may have more advantages than the sulfuric acid treatment, the sulfuric acid treatment has been chiefly adopted in the monazite industry of our country and will be used for some time henceforth, because

the technique of the latter has been cultivated for long time and the equipments have been constructed already.

In this paper, therefore, the process for recovering uranium from monazite in the sulfuric acid treatment is mainly described. This study was undertaken on Apr. 1954 and the process which had been improved by this investigation was adopted by Japanese uranium industry on Mar. 1955.

Monazite sand concentrate and its treatment in Japan

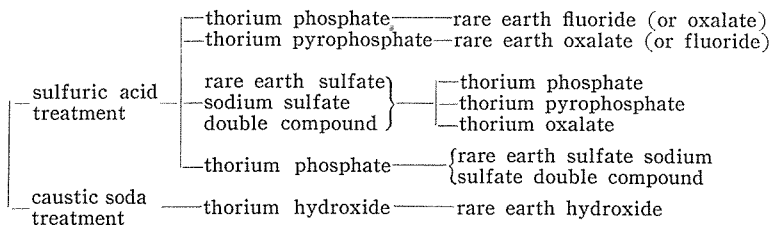
The chemical composition of the imported monazite sand concentrate is shown in Table 1.

Table 1. Composition of the imported monazite sand concentrate.

sample no.	1	2	3	4
locality	Tailand	Malay	Korea	Korea
ThO ₂	6.71	7.71	6.29	6.54
U ₃ O ₈	0.26	0.32	0.54	0.44
Ce ₂ O ₃ [La] ₂ O ₃	} 52.59	} 53.35	} 53.92	} 54.70
[Y] ₂ O ₃	2.75	3.27	2.75	1.69
Fe ₂ O ₃	2.11	2.26	1.42	3.85
Al ₂ O ₃	0.82	1.41	1.29	0.85
TiO ₂	1.93	1.17	1.00	0.83
CaO	0.65	0.94	2.06	2.16
MgO	0.41	0.24	0.79	0.53
ZrO ₂	0.54	0.46	0.31	0.54
SnO ₂	4.72	2.29	—	Nb ₂ O ₅ +Ta ₂ O ₅ 0.10
P ₂ O ₅	21.07	21.09	26.83	22.95
SiO ₂	5.31	5.66	4.31	5.28

The treatment of monazite was carried out in several ways according to the kinds of rare earth products and the requested grade of thorium content in them. The classification of monazite treatments from the standpoint of the separating method of thorium from rare earths, is described as follows.

Table 2. The classification of monazite treatment.



In the previous sulfuric acid treatment, uranium is almost transferred into the waste solution. The recovery of uranium from the waste solution is unfavorable from the economical stand-points, because a large amount of neutralization agent is required for the precipitation of uranium, in spite of the very dilute concentration of uranium. Therefore, the author has adopted the method by which uranium is precipitated with thorium in the separation process of thorium from rare earths. In the caustic soda treatment, uranium is precipitated with thorium by adjusting its pH.

Extraction of uranium salt from monazite

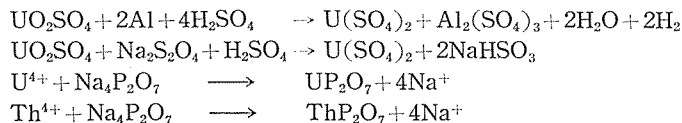
In the sulfuric acid treatment of monazite, it is unable to explain in details each method in this restricted paper. Therefore, as a representative instance, the uranium extraction method on the thorium pyrophosphate—rare earth oxalate treatment is described.

(I) Outline of process

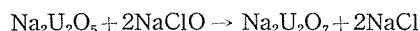
The process which has been developed as a result of the present investigation consists of the following operations and chemical reactions.

(i) Monazite is treated with conc. sulfuric acid and its decomposed material is dissolved in water.

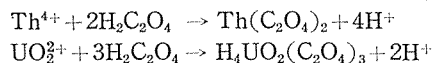
(ii) The extracted solution is treated with a reducing agent (metallic aluminium, hydrosulfite etc.), and to it sodium pyrophosphate solution is added.



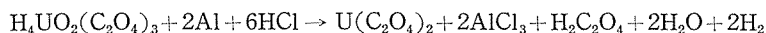
(iii) Pyrophosphate is treated with caustic soda solution and uranium (IV) is oxidized into uranium (VI) with sodium hypochlorite



(iv) Hydrous oxide (of uranium and thorium) is dissolved in conc. hydrochloric acid and oxalic acid solution is added to precipitate thorium oxalate alone.



(v) Then uranium (IV) oxalate is precipitated from the uranium complex solution by dissolving aluminium metal.



(vi) Uranium (IV) oxalate is converted into uranium trioxide by burning.

(II) Laboratory studies

(i) Decomposition of ore with sulfuric acid

Monazite sand concentrate was perfectly decomposed by heating at about 250°C

for 2 hr. with conc. sulfuric acid twofold the weight of monazite sand. Then the sulfate cake was dissolved into water tenfold the weight of monazite by stirring and settled over night. The extraction ratio of thorium, rare earth and uranium in this process arranged in 98~99 per cent to their content in original ore. The main composition of sulfuric acid solution of monazite is shown in Table 3.

Table 3. Main composition of sulfuric acid solution of monazite sand.

Constituent	Concentration, grams per litre
Th	4~7
U	0.3~0.6
Rare earth	45~60
Acid (sulfuric and phosphoric)	3~4N

(ii) Precipitation of pyrophosphate

The yield and purity of pyrophosphate are remarkably influenced by the following facts, that is, the acidity in the solution, the kind and quantity of reducing agents for uranium (VI) in the solution, the additional quantity of precipitant and the washing condition.

(1) Effect of acidity

In the synthetic solution which has nearly equal acidity to the extracted solution from monazite, the acidity was varied by diluting its volume to 3, 4, ..., 6 times with water. Hydrosulfite was used for the reduction of uranium (VI), and added 6 times the weight of uranium oxide in the solution. The result of the experiment which examined the relation between the acidity of solution and the resolution quantities of uranium and thorium is shown in Fig. 1.

According to it, in order to obtain more than 95 per cent of thorium precipitate from the extracted solution which contained over 6 gr. of ThO_2 per litre, it was necessary to dilute the original solution to at least 4 times.

(2) Effect of reducing agent

In the case of the reduction of uranium (VI) in acid solution, the best economical results were obtained by using metallic aluminium or hydrosulfite comparing with other several reducing agents. The relation between the added quantities

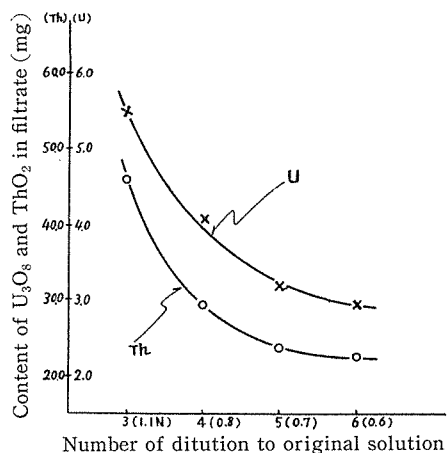


Fig. 1. Resolution quantities of uranium and thorium to various acidities.

Treatment—In 100 ml of solution which contained 165 gr. of H_2SO_4 and 37 gr. of H_3PO_4 per litre, 0.0210 gr. of U_3O_8 or 1.0319 gr. of ThO_2 was added, and the solution was diluted to various volumes. Then 45 ml of 5% $\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ was added in Th-contained solution and 10 ml in U-contained solution. Each precipitate was filtered and ThO_2 or U_3O_8 in the filtrate was analyzed.

of aluminium or hydrosulfite and the yield of uranium pyrophosphate is shown in Table 4. The chemical composition of the extracted solution used in the experiment was ThO_2 6.70, R_2O_3 59.02, U_3O_8 0.64, Fe_2O_3 0.93, TiO_2 0.41 and Al_2O_3 0.78 grams per litre, and acidity 4.0 N.

Table 4. Yield and purity of pyrophosphate to kind and quantity of reducing agent.

test no.	reducing agent			in pyrophosphate cake					U ₃ O ₈ and ThO ₂ in cake to these content of test sol.	
	kind	added (g)	soluble (g)	ThO ₂ (g)	U ₃ O ₈ (g)	R ₂ O ₃ (g)	Fe ₂ O ₃ (g)	TiO ₂ (g)	ThO ₂ (%)	U ₃ O ₈ (%)
1	Na ₂ S ₂ O ₄	2.0	2.0	6.350	0.041	0.185	0.190	0.085	94.8	6.4
2	"	3.0	3.0	6.387	0.048	0.212	0.093	0.085	95.3	7.5
3	"	4.0	4.0	6.342	0.216	0.207	0.030	0.084	94.7	33.8
4	"	5.0	5.0	6.389	0.464	0.230	0.026	0.085	95.3	72.5
5	"	6.0	6.0	6.390	0.575	0.240	0.015	0.084	95.4	90.0
6	"	7.0	7.0	6.410	0.572	0.273	0.015	0.084	95.7	89.4
7	Al	10.0	0.5	6.370	0.047	0.221	0.128	0.090	95.1	7.3
8	"	20.0	1.0	6.385	0.336	0.200	0.034	0.091	95.3	52.5
9	"	30.0	1.5	6.402	0.435	0.151	0.023	0.091	95.6	68.0
10	"	40.0	2.0	6.396	0.497	0.156	0.023	0.090	95.5	77.7
11	"	50.0	2.5	6.412	0.501	0.100	0.023	0.091	95.7	78.3

Treatment—In the case of using Na₂S₂O₄, after 1 litre of test solution was diluted to 4 times volume, various quantities of Na₂S₂O₄ were added, and then 300 ml of 5% Na₄P₂O₇ added. Precipitate was settled over night, filtered and twice washing carried out with 2 litre of water. The obtained cake was analyzed. In the case of aluminium, after various quantities of aluminium were immersed in 1 litre of test solution, reduced solution was diluted to 4 times volume with water and 300 ml of 5% Na₄P₂O₇ solution was added. The succeeding treatment has been carried out as mentioned above.

According to Table 4, in the case of hydrosulfite the most satisfactory results were obtained when 5 grams of hydrosulfite per litre of original solution were added. In the case of aluminium, it was necessary to immerse over night 40 grams of aluminium plate per litre. However, the quantities of these reducing agents were necessary to be increased corresponding to the increase of the amounts of iron (III) and cerium (IV) in the extracted solution. As is required hydrosulfite about 10 times as weighty as uranium in the extracted solution for the complete reduction of uranium (VI), it is undesirable economically to use hydrosulfite alone. According to the results of the experiments, the best economical result was obtained when 1 gram of hydrosulfite per litre of original solution was dissolved after 40 grams of aluminium per litre had been immersed over night.

(3) Effect of precipitant quantity

The experiment of the effect of precipitant quantity was carried out in the

same solution used in the experiment (2). The yields and purities of pyrophosphate cakes which were obtained by adding the various quantities of sodium pyrophosphate are shown in Fig. 2.

It has been reported²⁾ that thorium pyrophosphate and uranium (IV) pyrophosphate are soluble with the excess of sodium pyrophosphate in sulfuric acid solution. However, in the mixed acid solution of sulfuric acid and phosphoric acid, these phenomena were not recognized even when the precipitant 2 times as weighty as the thorium oxide equivalent was added and also when that 20 times as weighty as the uranium oxide equivalent was added.

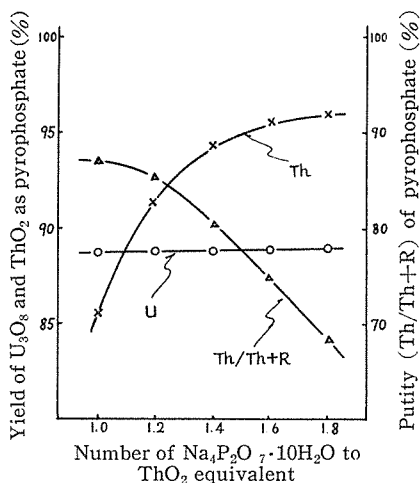


Fig. 2. Yields of uranium, thorium and rare earth as pyrophosphate to added quantities of sodium pyrophosphate.

Treatment—1 litre of test solution was diluted to 4 times volume and 6 gr. of $\text{Na}_2\text{S}_2\text{O}_4$ dissolved, then various quantities of 5% $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ added. After precipitate was settled over night and filtered by using the suction filter without washing. The obtained cake was analyzed.

in a dilute mineral acid. The result of the washing test on the pyrophosphate cake is shown in Table 5. The acidity of washing solution was adjusted to 0.1~0.3 N in which the solubilities of uranium pyrophosphate and thorium pyrophosphate can be disregarded.

Regarding the results of the experiments, in any case of hydrochloric acid, sulfuric acid or water, there was no difference among those quantities of rare earths removed. The ratio of thorium to thorium plus rare earth in pyrophosphate cake amounted to 90 per cent by the 1st washing and 95 per cent by the 2nd washing.

As shown in Fig. 2, it was recognized that uranium pyrophosphate precipitated prior to thorium pyrophosphate, since the yield of uranium pyrophosphate was constant independent of the additional quantities of precipitant in this range. Therefore, in the case of the solution which contains both uranium and thorium it is sufficient that only the precipitant of the estimated quantities to thorium content is added, without considering the uranium content. As the quantity of sodium pyrophosphate increased, the yield of thorium pyrophosphate increased, but on the contrary the purity of it decreased. Accordingly, it was found that the economical quantity of sodium pyrophosphate is 1.5 times as weighty as thorium oxide equivalent in the solution.

(4) Effect of washing

The unwashed pyrophosphate cake which was precipitated in the extracted solution involved the much rare earth pyrophosphate (Fig. 2). The rare earth pyrophosphate can be almost removed by the washing, because the rare earth pyrophosphate is easily soluble

Table 5. Effect of washing by various washing solutions.

test no.	washing sol.		in 1st washing sol.			in 2nd washing sol.			in washed cake		
	acidity (N)	vol. (l)	ThO ₂ (g)	U ₃ O ₈ (g)	R ₂ O ₃ (g)	ThO ₂ (g)	U ₃ O ₈ (g)	R ₂ O ₃ (g)	ThO ₂ (g)	U ₃ O ₈ (g)	R ₂ O ₃ (g)
1	0.15(HCl)	2	0.020	0.0005	3.270	0.012	0.0003	0.366	6.340	0.565	0.256
2	"	"	0.030	0.0004	3.100	—	—	—	6.410	0.572	0.273
3	0.30(H ₂ SO ₄)	"	0.012	0.0004	2.867	0.010	0.0003	0.446	6.360	0.562	0.308
4	"	"	0.015	0.0003	3.022	0.010	0.0003	0.352	6.310	0.505	0.240
5	H ₂ O	"	0.009	0.0003	3.079	0.005	0.0001	0.333	6.359	0.550	0.292
6	"	"	0.008	0.0003	2.975	0.005	0.0002	0.371	6.383	0.514	0.200

Treatment—Filtered thorium-uranium pyrophosphate which was precipitated with 300 ml of 5% Na₂P₂O₇ solution in 1 litre of test solution, was repulped in washing solution and filtered. The cake which had gone through 1st washing was repulped again in fresh washing solution and filtered. Main components of the obtained cake and each washed solution were analyzed.

(iii) Caustic soda treatment of pyrophosphate cake

The pyrophosphate cake was converted into hydrous oxide cake and trisodium phosphate solution by heating with a conc. caustic soda solution. From the various experiments seeking for the favourable reaction conditions, it has been clarified that the most satisfactory result was obtained under the following conditions, ratio of 1.5 caustic soda to cake, about 120°C in reaction temperature and about 2 hr. for reaction time. After the pyrophosphate cake had been reacted with caustic soda, the reaction mixture was diluted, maintaining approximately 100°C, with water to about 20 per cent sodium hydroxide concentration. Under these conditions, sodium orthophosphate remained in the solution. The slurry was filtered at 80°C to separate hydroxides of thorium and uranium from the sodium hydroxide-sodium phosphate solution. In order to reduce P₂O₅ content of cake to approximately 1 per cent the filtered oxides were washed twice with an equal volume of water with that of the diluted reaction slurry.

The oxidation of uranium (IV), which is required for the succeeding separation process of uranium from thorium with oxalic acid, was carried out with sodium hypochlorite at the second washing process. Because the oxidation in hydrochloric acid solution, which was brought in the succeeding process, was not adequate owing to the absence of the suitable oxidizing agent. The result of the experiment seeking for the relation between the oxidized degree of uranium (IV) and the quantity of the oxidizing agent is shown in Table 6.

The chemical composition of the pyrophosphate cake used in this experiment was ThO₂ 15.73, R₂O₃ 0.37, U₃O₈ (IV) 1.07, Fe₂O₃ 0.04, TiO₂ 0.21, P₂O₅ 13.07 and ignition loss 70.05 per cent. After 1 Kg of pyrophosphate cake had been treated with caustic soda under the condition previously mentioned, a series of thrice filtration and twice washing was set up. Before the 3rd filtration, the cake was repulped in hot water and the various quantities of 10 per cent sodium hypochlorite

Table 6. Degree of oxidation of uranium (IV) in cake to added quantities of 10% NaClO solution.

test. no.	added 10% NaClO (ml)	distribution of uranium			
		in Th-oxalate ppt.		in filtrate	
		U ₃ O ₈ (g)	Yield of U ₃ O ₈ (%)	U ₃ O ₈ (g)	Yield of U ₃ O ₈ (%)
1	10	1.396	13.05	9.232	86.28
2	20	0.600	5.61	10.085	93.51
3	30	0.341	3.19	10.344	97.67
4	40	0.283	2.04	10.410	97.29
5	50	0.275	2.57	10.281	96.08

Treatment—1 Kg of test pyrophosphate cake was treated under the condition described in this section. Hydrous oxide cake which had gone through the 1st washing was repluped in 3 litre of water and various quantities of 10% NaClO solution were added. After slurry was heated at 60°C for a little time and filtered, the obtained cake was dissolved in hydrochloric acid and treated under the condition of the next section mentioned. Main components of the obtained thorium cake and filtrate were analyzed.

solution were added to it. The oxidation degree of uranium (IV) in the final filtered cake was determined by the reaction of uranium (IV) and uranium (VI) with oxalic acid in the hydrochloric acid solution. According to Table 6, to oxidize completely uranium (IV) into uranium (VI) in the hydrous oxide cake, this oxidizing agent was expended three times as weighty as uranium in pyrophosphate cake.

(iv) Dissolution of hydrous oxide in hydrochloric acid, and separation of uranium from thorium with oxalic acid

In order to prepare a solution in which uranium and thrium could be separated with oxalic acid, several kinds of acid were investigated for dissolving the above mentioned hydrous oxides. To use nitric acid and sulfuric acid was inadequate because of obstructing the reduction of uranium (VI) on a later step. The best results were obtained when hydrochloric acid was used as the dissolving acid. Since the concentration of hydrochloric acid in the dissolving solution has influence not only upon the dissolution of the hydrous oxide cake, but also upon the yield and purity of thorium oxalate obtained on the next step, it is necessary to determine the quantities of hydrochloric acid considering both conditions of the dissolution of the cake and the reaction upon oxalic acid. The result of the experiment seeking for the relation between the quantities of hydrochloric acid and the yield and purity of thorium oxalate precipitate is shown in Fig. 3.

The chemical composition of the hydrous oxide cake used in this experiment was U₃O₈ 1.92, ThO₂ 27.22, R₂O₃ 2.10, Fe₂O₃+TiO₂ 4.06, P₂O₅ 1.64, SiO₂ 1.44 and ignition loss 59.77 per cent.

For the separation of thorium from uranium with oxalic acid the most desirable result was obtained when it was treated under the following conditions: 37%

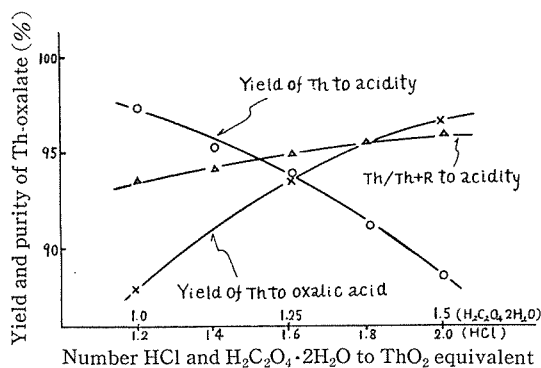


Fig. 3. Yield and purity of thorium oxalate to added quantities of hydrochloric acid and yield of thorium to quantities of oxalic acid.

Treatment—In the experiment referring to the quantity of hydrochloric acid, 1 kg of hydrous oxide was dissolved in various quantities of 37% HCl, diluted to twice volumes with water, filtered and added 350 gr. of H₂C₂O₄·2H₂O.

In the experiments to quantities of oxalic acid, 1 kg of the hydrous oxide was dissolved in 1 kg of 37% HCl. After solution was diluted to twice volumes and filtered, the various quantities of 10% H₂C₂O₄·2H₂O were added. The precipitates on each case was filtered, washed with water and dried. The obtained cake was analyzed.

hydrochloric acid 1.6 times as weighty as total metal oxide equivalent in the hydrous oxide cake was used, the acidity of the solution before the oxalic acid reaction was prepared by dilution with water of an equal volume to dissolved solution, and the quantities of oxalic acid were added 1.25 times as weighty as thorium oxide in the solution. In this process, the amount of uranium which was lost with thorium oxalate was 2~3 per cent to the total uranium in the hydrous oxide cake.

(v) Separation of uranium (IV) oxalate from filtrate

The important factors to separate the insoluble uranium (IV) oxalate by the reduction of uranium from the above mentioned filtrate which contained uranium (VI) oxalate complex, were the acidity of filtrate, the quantity of oxalic acid in the filtrate and the quantity of reducing agent added. The results of the experiments to seek the adequate acidity of solution and the sufficient quantity of oxalic acid for the uranium (IV) oxalate precipitation in the synthetic solution are shown in Fig. 4.

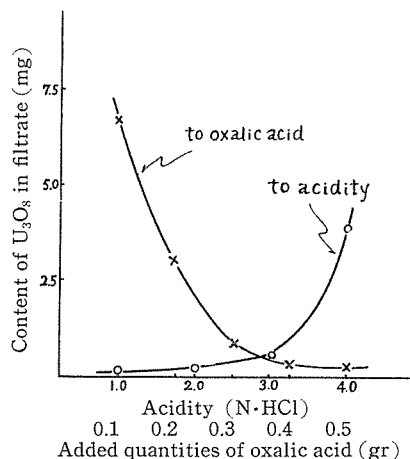


Fig. 4. Resolution quantities of uranium oxalate to added quantities of hydrochloric acid and oxalic acid.

Treatment—On the experiment of effect to quantities of oxalic acid, 0.0560 gr. of U₃O₈ was added in 100 ml of 2N HCl and then 1 gr. of Al was added. The separated uranium oxalate was filtered and U₃O₈ in the filtrate was analyzed. On the experiment to acidity of solution in the solution contained 0.0560 gr. of U₃O₈ and 0.3 gr. of H₂C₂O₄·2H₂O, various quantities of 37% HCl was added and its volume was measured to 100 ml. Then 1 gr. of Al was dissolved perfectly and separated uranium oxalate was filtered. U₃O₈ in filtrate was analyzed.

According to the results of the experiments, the suitable acidity of the solution, in which the precipitation of uranium oxalate occurred almost completely, was below 3 N. But, when it was below 1 N, the soluble rate of aluminium as reducing agent was too slow. The quantity of oxalic acid as precipitant of uranium was required at least 6 times as weighty as uranium oxide in the solution. In the actual filtrate from the thorium oxalate precipitation, its acidity showed about 1.5 N, and the excess of oxalic acid added as the precipitant of thorium in the previous process existed about 20 times as weighty as uranium oxide in the filtrate. Accordingly, the acidity and the quantity of oxalic acid in the filtrate have been already provided for the two conditions for separating uranium oxalate from the filtrate.

When aluminium was applied as a reducing agent, the relation between the added quantities of it and the yield of uranium oxalate is shown in Table 7. The concentration of the filtrate used was U_3O_8 1.300, $R_2O_3+ThO_2$ 0.061, Fe_2O_3 3.478, and TiO_2 0.312 gr. per litre, and acidity 1.5 N.

Table 7. Yield of uranium oxalate to added quantities of aluminium.

test no.	added Al (g)	content in uranium oxalate cake					U_3O_8 in U-oxalate cake to its content in test solution (%)
		U_3O_8 (g)	$ThO_2+R_2O_3$ (g)	Fe_2O_3 (g)	TiO_2 (g)	SiO_2 (g)	
1	1.0	0.8555	0.009	0.017	0.050	0.007	65.8
2	2.0	1.0310	0.007	0.018	0.039	0.009	79.3
3	3.0	1.1200	0.004	0.020	0.047	0.009	86.2
4	4.0	1.2485	0.003	0.019	0.056	0.007	96.0
5	5.0	1.2540	0.007	0.019	0.035	0.010	96.5

Treatment—Various quantities of aluminium were dissolved in 1 litre of test solution. The separated precipitate was settled until solution became clear, filtered and washed with water. The obtained cakes were analyzed.

According to Table 7, 4 gr. of aluminium per litre of filtrate was required for the perfect separating of uranium oxalate from the filtrate.

(III) Pilot-plant studies

In order to examine the adaptability of the above mentioned process on a large scale, a series of operation in pilot-plant equipment was carried out. The flow sheet of the process which has been improved is shown in Fig. 5.

(i) Treatment of monazite with sulfuric acid

The hemispherical cast-iron reaction vessel had a capacity of about 100 litres, and was settled on a coal furnace. 50 Kg of monazite ore and 100 Kg of conc. sulfuric acid were fed into the vessel for each one lot, then were heated with continuous agitation at 250~270°C, for 2 hr. This was sufficient time for complete decomposition of monazite sand. After complete reaction and cooling, the mixture was dissolved little by little with moderate agitation in water 10 times as weighty as sand.

The turbid solution was settled until the insoluble material completely descended. The concentration of a typical decantate is shown in Table 8.

(ii) Production of pyrophosphate cake

1,000 litres of the above mentioned decantate was poured into a reduction vessel, which was provided with 100 Kg of a vortical-shaped aluminium plate, with a help of acid proof pump, and settled over night. The reduced liquid was transferred into the reactor which had a capacity of about 5,000 litres, and diluted to 4 times the volume of the initial solution with water at the start of a run, which can be replaced at the second process by the washing process by pyrophosphate recycled from a later step. 1 Kg of hydrosulfite was added little by little with moderate agitation. Then, 20% sodium pyrophosphate solution involving 13 Kg of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ per 1,000 litres of the initial solution was added with vigorous agitation, and the slurry was settled over night. The desirable separation of rare earth from thorium and uranium could not be obtained unless the occluded solution and coprecipitated rare earth pyrophosphate were sufficiently removed from the solids by washing. For this purpose a series of three filtrations and two washings

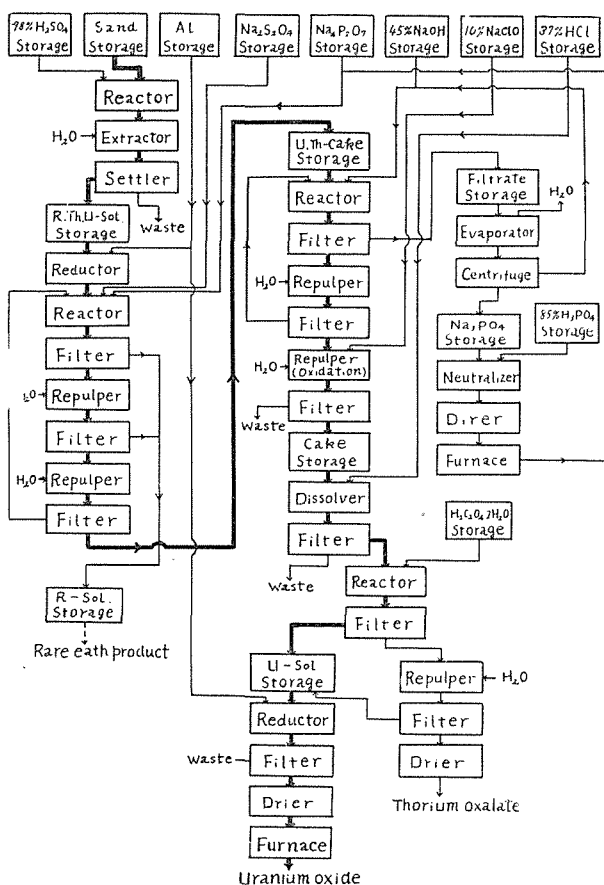


Fig. 5. Flow sheet for the recovery of uranium from monazite.

Table 8. Composition of typical decantate.

comp.	ThO ₂	R ₂ O ₃	U ₃ O ₈	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	acidity
(gr./l)	6.53	55.20	0.51	0.53	0.76	25.16	3.3N

was set up. As the washing solution, water was used and its volume was 1,000 litres at the 1st washing and 3,000 litres at the 2nd washing. Before each filtration, the slurry was settled and supernatant liquor was removed as much as possible by the decantation. After the first two filtrations, the cake was repulped and vigorously stirred in washing solution. The filtrations were performed with an overdriven bottom discharge centrifugal filter. The filtrate and decantate from initial slurry and the 1st washing slurry were combined, and offered to the production of rare earth compound. The combined filtrate and decantate from the 2nd washing slurry were recycled to the dilution of the abovementioned reduced liquor. The yield and composition of the pyrophosphate cake obtained in this process is shown in Table 9.

Table 9. Yield and composition of obtained pyrophosphate cake.

comp.	U ₃ O ₈	ThO ₂	R ₂ O ₃	Fe ₂ O ₃	TiO ₂	SiO ₂	P ₂ O ₅	ig. loss	H ₂ O
(%)	1.04	14.58	0.72	0.12	0.30	1.87	12.00	3.26	66.51

Yield—Pyrophosphate cake 42.5 Kg, U₃O₈ 0.44 Kg, ThO₂ 6.20 Kg and R₂O₃ 0.31 Kg

(iii) Caustic soda treatment of pyrophosphate cake and recovery of trisodium phosphate and caustic soda

The pyrophosphate cake was charged in a cast-iron reaction vessel with a commercial 45% caustic soda solution of an equal weight to the pyrophosphate cake (at the second process, with recovered caustic soda solution recycled from a later step), and heated to 120°C with moderate agitation. After the complete reaction, the mixture was diluted with water 2 times as much in volume as caustic soda solution used. The slurry was digested at about 100°C for 1 hr. to facilitate later filtration. After digestion the slurry was filtered keeping the temperature at 60°C up. The filtrate was stored to recover trisodium phosphate and caustic soda solution, and hydrous oxide cake was repulped, vigorously stirred in hot water and filtered to remove practically all the soluble elements in the cake. This filtrate was recovered for recycling as a diluent of the slurry at the beginning of this step. The cake was again repulped in hot water and then 10% sodium hypochlorite solution (30 gr. of 10% NaClO solution to 1 Kg of pyrophosphate cake) was added in it with moderate agitation. If the color of slurry was varied from greenish gray to yellowish gray, the slurry was filtered and its filtrate was wasted. An analysis of such a cake is given in Table 10.

Table 10. Composition of obtained thorium-uranium hydrous oxide cake.

comp.	U ₃ O ₈	ThO ₂	R ₂ O ₃	Fe ₂ O ₃ +TiO ₂	SiO ₂	P ₂ O ₅	ig. loss	H ₂ O
(%)	2.58	36.70	1.70	1.75	1.56	1.72	3.13	50.30

Yield—thorium-uranium hydrous oxide 16.9 Kg

The filtrate stored to recover trisodium phosphate and caustic soda was concentrated by evaporation in an open steel kettle until the boiling temperature reached 135°C during agitation. The separated trisodium phosphate crystal and 47% sodium hydroxide solution were divided by filtration. The recovered caustic soda liquor was recycled to the pyrophosphate reaction, and trisodium phosphate was offered to produce sodium pyrophosphate after it was upgraded by neutralization of the contained sodium hydroxide with phosphoric acid.

(iv) Dissolution of hydrous oxide cake in hydrochloric acid and production of thorium oxalate cake

The hydrous oxide cake was placed in the acid-dissolution vessel fitted with 2 KW heater. To it was added 37% hydrochloric acid of an equal weight to the cake. The mixture was heated at about 80°C for 1 hr., and diluted to twice volume with water. Insoluble materials, which consist mainly of silica, were filtered using rubber lining filter and washed with water. The acid solution was transferred into the reaction vessel and 20% oxalic acid solution containing 1/2 Kg of oxalic acid crystal to 1 Kg of the hydrous oxide cake was added with moderate agitation. The slurry was heated at about 60°C for 1 hr. and settled over night. The precipitate was filtered with rubber lining centrifugal filter after removing the supernatant liquor as much as possible. The wet cake was repulped in water and the repulped slurry was settled again, decanted and filtered. The decantate and filtrate combined with the liquors from the first filtration were offered to the extraction of uranium. The yield and composition of the obtained thorium oxalate are shown in Table 11.

Table 11. Yield and composition of obtained thorium oxalate cake

comp.	ThO ₂	R ₂ O ₃	U ₃ O ₈	Fe ₂ O ₃	TiO ₂	SiO ₂	ig. loss	H ₂ O
(%)	22.02	0.72	0.03	0.07	0.27	0.32	19.06	57.23

Yield—Thorium oxalate 25.3 Kg, ThO₂ 5.57 Kg and ThO₂ in thorium oxalate to its content in original ore 85.3%

An extremely pure thorium product could be obtained from this cake by the purification process.

(v) Production of uranium oxalate

The combined decantates and filtrates stored to recover uranium were transferred into an acid-proof vessel. To it was added aluminium scrap (5 Kg of scrap to 1,000 litres of the liquor). The solution was stirred every five minute to dissolve aluminium completely. After the dark greenish uranium oxalate precipitate was completely separated, the slurry was decanted and then filtered with suction filter. At the completion of filtration, the oxalate cake was washed in the filter with water until the soluble elements in the cake were removed almost entirely. The wet uranium oxalate cake was oven-dried at 100°C and the filtrate and decantate were wasted. The yield and composition of the wet uranium oxalate obtained in this process are given in Table 12.

Table 12. Yield and composition of obtained uranium oxalate cake.

comp.	U ₃ O ₈	ThO ₂ +R ₂ O ₃	Fe ₂ O ₃	TiO ₂	Al ₂ O ₃	SiO ₂	ig. loss	H ₂ O
(%)	20.26	1.42	0.32	1.46	0.30	0.85	12.98	61.86

Yield—Uranium oxalate 19.8 Kg, U₃O₈ 0.40 Kg and U₃O₈ in uranium oxalate to its content in original ore 78.4 %

The dried oxalate cake was placed in a chamotte burning vessel and burned at 400°C for 3 hr. in an electric furnace. The obtained uranium oxide was dissolved in nitric acid and could be purified by solvent extraction or ion exchange process.

Conclusion

According to the process which has been investigated by the author, uranium and thorium can be extracted as the by-product in the process of rare earth production from monazite. In this case the yield of uranium was more than 75 per cent to its content in the original sand and that of thorium was more than 85 per cent. They are sufficient as by-products. This process had the following characteristics.

(1) Both uranium and thorium can be separated from rare earth with sodium pyrophosphate almost without being accompanied by rare earth at an initial step of a run.

For the purpose of the separation of uranium from rare earth at this step, the operation, which is added to the process which has been hitherto applied, is the reduction operation of uranium (VI) alone in acid extracted solution.

(2) By the conversion of atomic valency of uranium in the same solution, a series of operations for the separation of uranium from thorium and the precipitation of uranium is carried out with oxalic acid alone.

The operations succeeding to the hydrochloric acid dissolution in this process can be applied also to the hydrous oxide cake from caustic soda treatment of monazite sand.

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