The Seperation and Purification of Rare Earth Elements from Monazite (I)

By Hisaichi ARAKAWA

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The separation of rare earth elements is particularly difficult on the large scale in the industrial process, and the usual commercial method of separating these elements in their mixture obtained from monazite ores requires large quantities of oxalic acid, ammonium oxalate and special reagents, which are difficult to obtain in this country. Therefore the author investigated a new method that does not require oxalates and other special reagents.

1. Materials. The new materials used in this investigation were monazite from Sengan, in Korea. The composition of two samples are shown in Table 1.

Table 1.

No.	$ThO_2 + R_2O_3$	ThO_2	P_2O_5	MgO	CaO	Al_2O_3	Fe_2O_3	SiO_2	Ignition loss	H_2O	total
	%	%	%	%	%	%	%	%	%	%	%
1.	64.03	6.70	23 61	0.74	0.57	1.38	7.48	3.00	—	—	100.81
2.	61.44	6.52	13.80	0.08	4.95	19.50		2.10	0.56	0.32	102.7

2. Extraction of thorium and rare earths from monazite: For the decomposition of monazite, there are several methods, such as the sulphuric acid method, the carbon method, or the method by alkali-fusion.

The author, at first, studied the sulphuric acid method.

Powdered monazite in concentrated sulphuric acid is heated to render thorium and rare earth soluble in water. After cooling, it is slowly mixed with cold water and allowed to stand overnight. It is then filtered. The filtrate contains thorium and rare earths, iron, aluminium, phosphoric acid, etc. The representative methods in which thorium and rare earths are separated from one another and from other elements in the extracted solution are as follows:

(a) The fractional precipitation of thorium phosphate, as a white isinglasslike precipitate, produced upon addition of ammonia water or magnesia to the extracted solution.

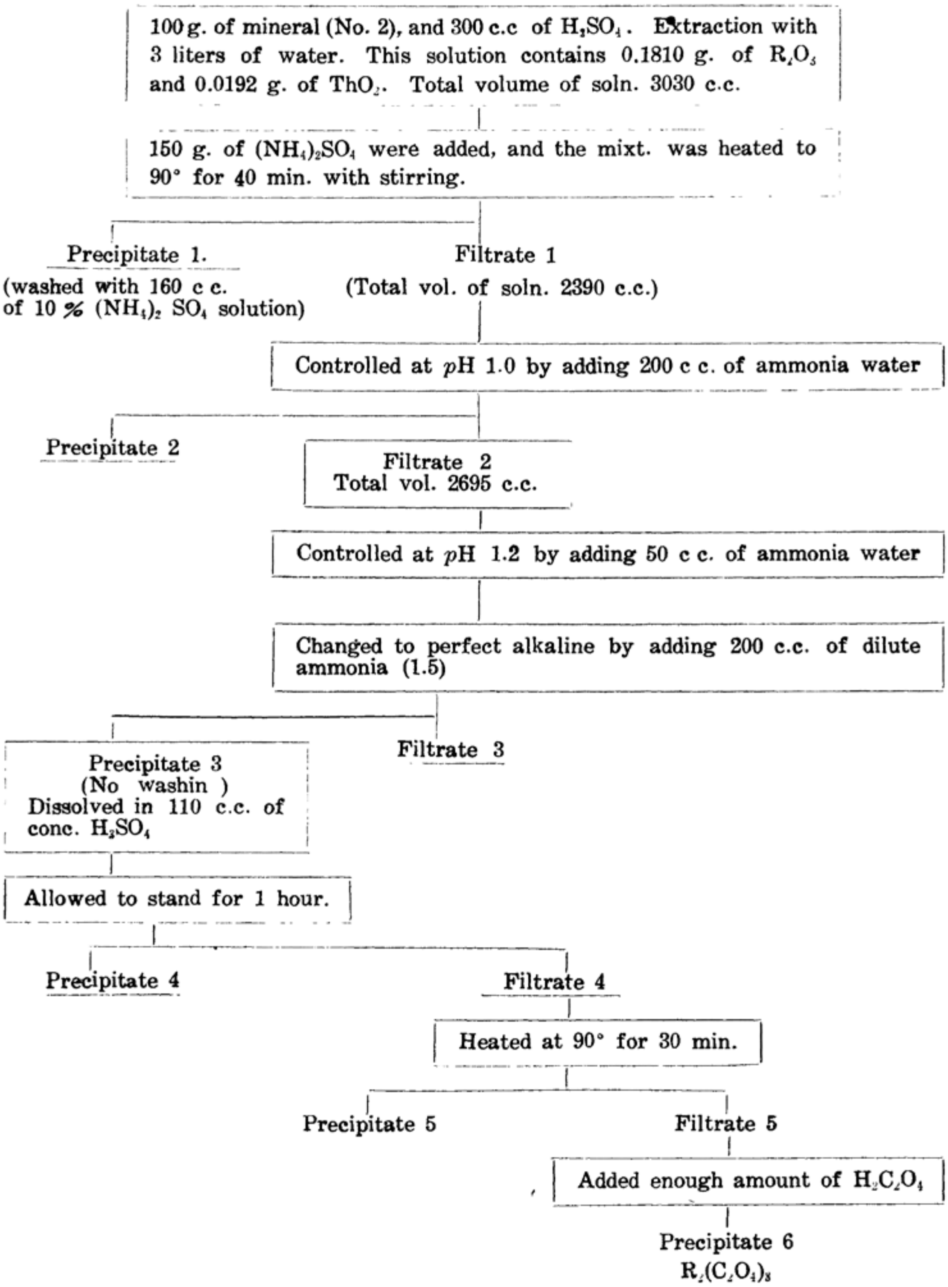
(b) The removal of the cerium group rare earths double compound of alkali sulphate, produced by addition of the reagent to the extracted solution.

In the past, method (a), using ammonia or magnesia, was used in industry. Method (b) has been adopted recentry, especially for the treatment of monazite of low thorium content. The author carried out a few experiments on the two methods. As the results, it is seen that in separating thorium from rare earths by fractional precipitation with ammonia, when pH is controlled at 1.0, precipitate of thorium compound having the purity ($ThO_2/ThO_2+R_2O_3$) of 93% was obtained (yield 60%). When the pH was controlled at 1,2, the purity was 86% and yield 80%. However, the composition of the precipitate changes remarkably due to slight change of pH. The precipitate is voluminous, and is difficult to filter.

In the method by the adition of sodium sulphate or sodium chloride and sulphuric acid, the precipitate was not difficult to filter but the efficiency for separation from one another was considerably inferior to the above method.

3. Separation of rare earths from the extracted solution as ammonium rare earths sulphate compound. The author tried to separate rare earths from the extracted solution as ammonium rare earths sulphate compound in order to improve the defects of the method of fractional precipition by ammonia. This compound is a pink crystal and is produced ahead of thorium phosphate when the concentration of the extracted solution is above a certain value. Its composition war found to be $(NH_4)_2SO_4 \cdot R_2(SO_4)_3 8H_2O$. This double compound is produced in larger amounts at higher temperature than at room temperature. The precipitate which is produced at higher temperature is in the form of small particles and is difficult to filter. Therefore, it is better to keep the solution at room temperature and make the precipitate grow as much as possible, and then to precipitate the remaining rare earths as small particles at higher temperature. About 63% of rare earths, which is free from thorium, can be separated. Considering that 37% of rare earth remains in the solution, the author attempted to separate th rare earths by adding more ammonium sulphate and heating to 90°C. A brilliant white precipitate was formed but it contained considerable amounts of thorium. The relative concentration of thorium in the filtrate, after the recovery of 63% rare earths, has been raised. When

Table 2.



100 g. of mineral (No. 2), and 300 c.c of H_2SO_4. Extraction with 3 liters of water. This solution contains 0.1810 g. of R_2O_3 and 0.0192 g. of ThO_2. Total volume of soln. 3030 c.c.

150 g. of $(NH_4)_2SO_4$ were added, and the mixt. was heated to 90° for 40 min. with stirring.

Precipitate 1. (washed with 160 c c. of 10 % $(NH_4)_2SO_4$ solution)

Filtrate 1 (Total vol. of soln. 2390 c.c.)

Controlled at *p*H 1.0 by adding 200 c c. of ammonia water

Precipitate 2

Filtrate 2 Total vol. 2695 c.c.

Controlled at *p*H 1.2 by adding 50 c c. of ammonia water

Changed to perfect alkaline by adding 200 c.c. of dilute ammonia (1.5)

Precipitate 3 (No washin) Dissolved in 110 c.c. of conc. H_2SO_4

Filtrate 3

Allowed to stand for 1 hour.

Precipitate 4

Filtrate 4

Heated at 90° for 30 min.

Precipitate 5

Filtrate 5

Added enough amount of $H_2C_2O_4$

Precipitate 6 $R_2(C_2O_4)_3$

fractional precipitation by adding ammonia to the filtrate was done and *p*H of the solution was controlled, a white isinglasslike precipitate was prduced. It was almost free from cerium. The filtrate from the above precipitate was controlled to *p*H 1.2, and it produced a white amorphous precipitate, in which the ratio $ThO_2/ThO_2+R_2O_3$ was 0.27. Then this precipitate was filtered off, and the filtrate was controlled to *p*H 2.0. It produced a white precipitate, which contained no thorium. Therefore the above procedure is simple and gives better results than a method of direct fractional precipitation by addition of ammonia. It can be shown as follows (Table 2).

The weight and composition of obtained precipitates are shown in Table 3.

Table 3.

No. of ppt.	Weight of ppt.	Composition	R_2O_3 in the ppt.	$ThO_2/ThO_2+R_2O_3$	Rate of recovery
1	62.5 g.	$(NH_4)_2SO_4R_2(SO_4)_3$ $8H_2O$	25.4 g.	0 %	51.9 %
2	158 g.	Th-phosphate & R-hydroxide	1.5 g.	66.7	3.1
3	67 g.	Same to the above	2.97 g.	29.9	6.05
4	37 g.	$(NH_4)_2SO_4R_2(SO_4)_3$ $8H_2O$	15.1	0	30.9
5	4 g.	Same to the above	1.6	0	3.3
6		$R_2(C_2O_4)_3$	1.4	0	2.8

4. Separation of cerium from the rare earths ammonium sulphate double salt. Cerium is present in the double compound only in trivalent cerous form. In solution this may be oxidized to tetravalent ceric from, by ammonium persulphate, permanganate etc.

When the acidity of the resulting solution is decreased by adding dilute ammonia, a yellow precipitate of ceric-oxy-sulphate forms. The author tried to follow this plan to separate cerium from the other rare earths and to investigate the quantities of the reagent required for the most favorable separation. In the first investigation, experiments were performed to determine the quantities of ammonium persulphate necessary to completely oxidize the cerous cerium to ceric. According to the rerults of the experiments, the quantity of ammonium persulphate required is seven times the theoretical quantity. In the investigation in which the oxidized cerium was precipitated by ammonia, the relation of (1) the quantity of ammonia, (2) the purity of the precipitate and (3) the percentage of recovered cerium, was studied.

Experiment performed: The solution used in this investigation had the composition shown in Table 4. To 25 c.c. of this solution various quantities (25.0, 25.5, 26.0, 26.2, 26.5 and 27.0 c.c.) of 1.022N ammonia were added. The mixtures were permitted to stand overnight and then filtered. The precipitates were analysed immediately without washing. The results are shown in Table 5.

Table 4

C··· + Ce····	8.0 mg/c.c.
Ce····	7.4 mg/c.c.
Oxidizing rate	92.5%
R_2O_3	16.2 mg/c.c.
Free acidity	2.49N.

Table 5.

No.	1	2	3	4	5	6
Added amount of ammonia (c.c.)	24.0	25.5	26.0	26.2	26.5	27.0
Yield of Ce (%)	65	69	69.5	75	87	100
Purity of Ce	86	87	93	95	87	69
*p*H	2.07	2.13				

As is evident from this table, the relation of purity and yield of cerium was not strictly reverse, but a point of maximum of purity exists when a certain definite amount of ammonia was added.

Next the author tried the following experiment in order to reexamine " this point " and to investigate the effect of adding smaller quantities of more coucentrated ammonia solution. In this experiment the precipitates were washed with distilled water. A saturated aqueous solution of the double compound was prepared and a few drops of sulphuric acid were added to prevent hydrolysis. It contained 93.7 mg. of CeO_2 per 10 c.c. with a free acidity of 1.64N. Ammonia solution (1.96N) was added into 25 c.c. of the solution drop by drop. When about 21 c.c. of ammonia was added to the first portion, precipitates began to appear. Similar experiments were performed using 21.10, 21.55, 21.86, 22.00, 22.40 and 22.70 c.c. of ammonia respectively. After the ammonia was added, the samples were allowed to stand for 1 day and then filtered. The results of the experiments are shown in Table 6.

Table 6.

No.	1	2	3	4	5	6
Added amount of ammonia (c.c.)	21.10	21.55	21.86	22.00	22.40	22.70
Yield of Ce (%)	66.0	66.5	72.2	77.8	91 4	99.3
Purity of Ce (%)	93.0	94.4	96.7	95.2	94.1	83.2
*p*H	1.82	1.84	1.87	2.12		5.90
Colour of soln.	yellow	yellow	⊙colourless	,,	,,	,,

⊙ The filtrate of the solution of ammonium rare earths sulphate, from which 70% of cerium had been separated, contained 30 % of cerium notwithstanding the fact that the solution was colourless, but when sulphuric acid was added to the colourless solution, distinct colour appeared.

Summary. (1) The rare earths, free from thorium, could be separated as the earths sulphate double compound (yield 93%).

(2) The method of separating thorium from the filtrate, which was obtained by separating about 63% of rare earths salt from the extracted solution, gives better result than a method of direct fractional precipitation from the extracted solution.

(3) Cerium can be separated from a solution as rare earths ammonium double compound with a purity of 92—96% (yield 70—75%).

(4) In the separation of cerium, a maximum point of purity is obtained when sufficient quantity of ammonia is added just to remove the colour of Ce ion from the solution. The purity and yield of cerium is not strictly in an inverse proportion, but a point of maximum purity of precipitate is obtained when a certain definite amount of ammonia is added.

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