

EXTRACTION OF RARE EARTHS FROM MONAZITE SAND

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EXTRACTION OF RARE EARTHS FROM MONAZITE SAND  
RARE EARTH RESIDUES.

Introductory.

More than three thousand tons of monazite sand are decomposed annually in order to obtain the thorium necessary for the manufacture of incandescent gas mantles. Since monazite is primarily a phosphate of the cerium group metals of the rare earths and as the percentage of thoria is usually quite low, very large quantities of compounds of this group are annually produced during the process of extraction of thorium. Such compounds are known as monazite residues, and are usually in the form of double carbonates or double sulphates.

These residues have been extensively used by rare earth workers as a source of cerium group elements. Although they are widely used, little information is available as to the methods of extraction of rare earths from them. A little more is known regarding the decomposition of the original ores, although these are not nearly so widely used as are the residues.

James, in his "A Scheme for the Separation of Rare Earths,"<sup>(1)</sup> suggests the following method for the decomposition of an ore:- The mineral is decomposed either by hydrochloric acid, sulphuric acid, potassium bisulphate,

sodium hydroxide or hydrofluoric acid. When hydrochloric acid is used, the whole is evaporated to dryness to render the silica insoluble, and then warmed with a little concentrated hydrochloric acid, after which the mass is treated with water and filtered. The filtrate may then be precipitated either by oxalic acid or ammonium oxalate. When sulphuric acid or potassium bisulphate has been used to break up the mineral, it is necessary to stir with cold water to obtain solution of the desired elements. Fusion with sodium hydroxide and washing with water gives a residue of oxides. These are dissolved in hydrochloric acid.

Hydrofluoric acid decomposes many minerals in the cold, giving a residue of rare earth fluorides. The insoluble fluorides are decomposed by means of sulphuric acid. The sulphate or chloride solutions are then precipitated either by ammonium oxalate or oxalic acid.

James<sup>(2)</sup> has digested euxenite with strong sulphuric acid. He has decomposed fergusonite and samarskite with hydrofluoric acid, or with concentrated sulphuric acid containing potassium sulphate to raise the temperature. He fused columbates for two hours with twice its weight of sodium hydroxide, while he digested yttrotitanite and gadolinite with hydrochloric acid and ytterspar with an equal weight of sodium hydroxide plus half its weight of water.

Prandtl and Loesch<sup>(3)</sup> attacked monazite earth with concentrated nitric acid. Wenger and Christin<sup>(4)</sup> recommend concentrated sulphuric acid for this purpose.

Chesneau<sup>(5)</sup> fused monazite with sodium potassium carbonate.

Hicks<sup>(6)</sup> used sulphur monochloride for opening up rare earth minerals containing columbium, tantalum, titanium, etc. Travers<sup>(7)</sup> fused one gram of finely powdered zirconium mineral with ten grams of sodium peroxide.

On the other hand, the only available reference to the decomposition of monazite residues is that of Hopkins and Kremers<sup>(8)</sup>. They advise boiling double sulphates for a few hours with a fifty per cent sodium hydroxide solution, until they are completely disintegrated. The mass is then diluted and the resulting hydroxides filtered and washed with boiling water until free from sulphates. The hydroxides are then dissolved in nitric acid, and the rare earths precipitated from hot solution by means of oxalic acid.

It is noteworthy, however, that in no case has any quantitative work been conducted in order to ascertain which method of extraction would yield the maximum possible results.

Since, therefore, the monazite residues formed the source of so much material used in the cerium group rare earth work, and in as much as the presence of illinium was first detected in such residues, (cf. Harris-Hopkins<sup>(9)</sup>), and as this is the first of a series of investigations regarding the concentration of this element, it was deemed advisable to investigate quantitatively, methods that would

yield maximum extraction of all rare earths present.

#### Analysis.

The materials used in this work were finely powdered sodium cerium-group sulphates. In order to check the efficiency of the various methods of extraction, the material was analyzed, first according to a method proposed by W.F. Hillebrand<sup>(10)</sup>, and then by a method which was devised and found to be more adaptable. Both methods are given below.

Two gram samples of the material were fused with excess sodium carbonate, the melt digested with water containing a few drops of methyl alcohol, filtered, and the precipitate washed with water until the filtrate did not affect red litmus paper. The precipitate was washed into a beaker with 100 c.c. of dilute sulphuric acid, digested on the hot plate and filtered through the original filter paper. The filter paper and undissolved precipitate were then ignited. The resulting oxides were fumed with hydrofluoric and concentrated sulphuric acids, dissolved in dilute sulphuric acid and the solution filtered. The two filtrates thus obtained were made alkaline with potassium hydroxides to precipitate the rare earths and ferric and titanic oxides (if any) while retaining the silica and alumina in solution. The precipitate was allowed to settle; the liquor poured off and the precipitate washed by decantation, filtered and again washed slightly on the filter paper. The precipitate

was then washed from the paper into a small platinum dish, treated with hydrofluoric acid and the liquid evaporated nearly to dryness. A little water with a few drops of hydrofluoric acid was added and the insoluble rare earth fluorides (crude) were collected on a small filter paper held by a waxed funnel. The precipitate was washed into a small platinum dish and evaporated to dryness with sulphuric acid, the paper being burned and added before expulsion of the acid. The sulphates were dissolved in dilute hydrochloric acid, the rare earth hydroxides precipitated by ammonium hydroxide, redissolved in hydrochloric acid, the solution evaporated to dryness and the residue heated with a few cubic centimeters of oxalic acid. The mixture was filtered, the precipitate ignited and the resulting oxides weighed.

0.7880 grams rare earth oxide were extracted from 2.0000 grams of the original material by the above method of Hillebrand.

In another determination, the method of analysis used was as follows: After precipitating the soluble sulphates with potassium hydroxide, the resulting hydroxides were transferred to a platinum dish, the filter paper ignited and added, and the whole fumed with concentrated sulphuric acid. The sulphates were dissolved in dilute sulphuric acid, the rare earth hydroxides precipitated by ammonium hydroxide, dissolved in hydrochloric acid, the solution evaporated to dryness and the residue heated with a few cubic centimeters

of oxalic acid. The mixture was filtered, the precipitate ignited and the resulting oxides weighed.

Two samples were analyzed by the above method. In the first, 0.3944 grams were extracted from 1.0000 gram, and in the second, 0.7860 grams of rare earth oxide were extracted from 2.0000 grams of the original material.

Results of analysis.

Method of Analysis	Wt. of Monazite residue	Wt. of $R_2O_3$	Wt. $R_2O_3$ per 100 grams monazite residue
Hillebrand	2.0000 grams	0.7880 grams	39.40 grams
Modified	1.0000 "	0.3944 "	39.44 "
Modified	2.0000 "	0.7860 "	39.30 "

The modified method is less troublesome, and from the above figures appears to be quite as accurate as the longer one.

Acid Extraction.

Although one would not expect maximum results by means of acid extraction, it was thought that it would be interesting to compare the efficiency of the mineral acids as extractants. Accordingly, two gram samples of the original residues were digested with nitric, hydrochloric and sulphuric acids. In each case the two gram sample was digested with 25 c.c. of concentrated acid, evaporated to 5 c.c., taken up in 250 c.c. water, boiled and filtered.



The sulphuric acid solution was cooled before filtering.

In addition, two gram samples were digested with excess saturated sodium hydroxide solution as in the method of Hopkins and Kremers<sup>(8)</sup>. The resulting hydroxides were boiled with 50 c.c. of concentrated nitric acid, evaporated to 10 c.c., taken up in 600 c.c. water, boiled and filtered.

Concentrated oxalic acid was added to each of the above filtrates. The resulting oxalates were filtered off, ignited and weighed as the oxide.

The following table shows the weights of rare earth oxide thus obtained.

Digested with	Sample	Wt. R <sub>2</sub> O <sub>3</sub> from 2 g.	Wt. oxide extracted per 100 grams monazite residue.
HNO <sub>3</sub>	I	0.3146 grams	15.73 grams
	II	0.2252 "	11.26 "
HCl.	I	0.5814 grams	29.07 grams
	II	0.5070 "	25.35 "
H <sub>2</sub> SO <sub>4</sub>	I	0.7975 grams	39.87 grams
	II	0.6870 "	34.35 "
NaOH	I	0.7778 grams	38.89 grams
	II	0.7595 "	37.98 "

From these values it appears that there is little difference between sodium hydroxide and sulphuric acid on small samples.

Application of the above methods to large amounts of material, however, showed that none of the acid extractions were applicable, giving widely varying results, and two weeks digestion with acid served to remove only a very small portion of the material present. Extraction with sodium hydroxide solution was also not very satisfactory. 1483 grams of rare earth material were boiled with excess concentrated sodium hydroxide solution. The resulting hydroxide precipitate was fumed with concentrated sulphuric acid and the soluble sulphates dissolved in water. Concentrated oxalic acid was added to the sulphate solution and the precipitated rare earth oxalates dried and weighed. Two gram samples of the dried oxalate were ignited and weighed and from this value, the weight of rare earths as the oxides calculated

Results of NaOH digestion.

Wt. monazite residue decomposed	1483 grams
Wt. rare earth oxalate obtained	544 "
Wt. oxide from 2 g. oxalate	1.0000 "
Wt. $R_2O_3$ extracted per 100 g. monazite residue	18.34 "

Fusion Methods.

It was then decided to try out the efficiency of fusion methods, using alkali fusions as being the most likely to be successful. Sodium hydroxide and sodium car-

bonate were the two fusion reagents used.

Four two gram samples of the original material were fused with four grams of sodium hydroxide. The melt was boiled with 200 c.c. of water and filtered.

Sample (1). The oxide residue was digested with 125 c.c. of dilute nitric acid, made up to 600 c.c. with water, boiled and filtered. The undissolved nitrate residue was digested with concentrated nitric acid, diluted with water, boiled and filtered.

Sample (2). This oxide was digested with 125 c.c. of concentrated nitric acid, diluted to 600 c.c. with water, boiled and filtered. The undissolved residue was again digested with concentrated nitric acid.

Sample (3). This oxide was digested with 125 c.c. of dilute sulphuric acid, made up to 900 c.c. with water and filtered. The undissolved sulphate residue was fumed with concentrated sulphuric acid, taken up in water, boiled, cooled and filtered.

Sample (4). This oxide residue was digested with 125 c.c. of concentrated sulphuric acid, evaporated almost to dryness, taken up in 500 c.c. of water, boiled, cooled and filtered. The sulphate residue was digested with 400 c.c. of water and the residue from this treatment again fumed with sulphuric acid and taken up in 800 c.c. of water.

Excess concentrated oxalic acid was added to the nine filtrates from the above treatments and the insoluble rare earth oxalates filtered off, ignited and weighed.

Below are the weights of rare earth oxides obtained in this manner.

Sample	Wt. oxide from 2 g. residue	Wt. oxide ext. per 100g. residue.
I. Digestion of oxide with dil. $\text{HNO}_3$	0.3611 g.	18.05 g.
Digestion of above residue with conc. $\text{HNO}_3$	0.2880 g.	14.40 g.
Total Oxide	<u>0.6491 g.</u>	<u>32.45 g.</u>
II. Digestion of oxide with conc. $\text{HNO}_3$	0.5981 g.	29.90 g.
Digestion of above residue with conc. $\text{HNO}_3$	<u>0.1281 g.</u>	<u>6.41 g.</u>
Total Oxide	0.7262 g.	36.31 g.
III. Digestion of oxide with dil. $\text{H}_2\text{SO}_4$	0.4948 g.	24.74 g.
Digestion of above residue with conc. $\text{H}_2\text{SO}_4$	<u>0.1816 g.</u>	<u>9.08 g.</u>
Total Oxide	0.6764 g.	33.82 g.
IV.. Digestion of oxide with conc. $\text{H}_2\text{SO}_4$	0.5121 g.	25.61 g.
Digestion of above residue with water	0.2304 g.	11.52 g.
Digestion of above residue with conc. $\text{H}_2\text{SO}_4$	<u>0.0387 g.</u>	<u>1.93 g.</u>
Total Oxide	0.7812 g.	39.06 g.

Two two gram samples were fused with four grams of sodium carbonate (anhydrous). The melt was digested with 200 c.c. of water, filtered and washed, ignited with the filter paper, fumed with concentrated sulphuric acid, taken up in 400 c.c. of water, boiled, cooled and filtered. The soluble rare earth sulphates were precipitated by oxalic acid, filtered, ignited and weighed.

Results of Na<sub>2</sub>CO<sub>3</sub> fusion.

	Wt. oxide from 2 g. residue	Wt. oxide extraction per 100 g. residue
Sample (1)	0.5951 grams	29.76 grams
Sample (2)	0.6154 "	30.77 "

The above values from the sodium carbonate fusion are probably lower than they would have been if the precipitate from the water digestion had not been ignited. This lowering is due to the fact that ignited rare earth oxides containing cerium are difficultly soluble in any acid.

The following method of extraction was finally tried on a larger scale and found to be most satisfactory:-

Equal weights of monazite residue and soda ash are mixed, poured into a Battersea crucible, fused in a muffle furnace and while still molten, poured into water. The crucible is immediately charged again, placed in the furnace and the operation repeated.

The molten mass is completely disintegrated by the sudden cooling. It is filtered, and washed with water until

the filtrate does not affect red litmus paper. The precipitate is dried on a steam bath, made up to a thin paste with concentrated sulphuric acid and evaporated almost to dryness, when copious white fumes begin to come off. The resultant sticky mass is digested with water and the soluble sulphates precipitated as oxalates by oxalic acid. The residue is digested with more water and the soluble sulphates precipitated as oxalates. This is repeated until only a minute quantity of oxalate is precipitated from 5 litres of the solution. From time to time a few drops of sulphuric acid are added to the sulphate material to keep the solution slightly acid.

In the first run, 872 grams of original material were fused with 1474 grams of  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$  and 580 grams of dried rare earth oxalates were extracted.

In the second run, 2000 grams of monazite residue were mixed with 2000 grams of soda ash. The material was fused, washed and heated with concentrated sulphuric acid until it became quite pasty. Five litres of water were added and the mixture heated and stirred. The liquor was decanted and filtered. The filtrate was deep red in colour and was marked filtrate (1). Another five litres of water were added to the residue and again a red filtrate was obtained. The filtrates from the third and succeeding washings were quite colourless. In all, the residue was washed twelve times and filtrates (1) - (12) obtained. Five litres of water were then added to the residue which was

set aside for nine weeks, water being added to make up for loss by evaporation. It was then filtered and the colourless solution marked filtrate (13). Excess concentrated oxalic acid was added to the filtrates and the insoluble rare earth oxalates precipitated, filtered dried and weighed. Oxalates (5) - (12) were united.

Oxalate (1) was decidedly pink. The red colouration gradually decreased in intensity from oxalate (1) to oxalate (13) which was almost pure white.

Two gram samples of the oxalates were ignited to oxides and weighed, and from this the weight of rare earths calculated as the oxide. Below is a table of the values obtained from the extraction of 2000 grams of monazite residues.

Oxalate	Wt. Oxalate	Wt. oxide from 2 g. oxalate	Average wt. from 2 g. oxalate	Total wt. of oxide from oxalate
I	376.55 g.	0.9535 g. 0.9558 g.	0.9542 g.	179.8 g.
II	881.60 g.	0.9813 g. 0.9847 g.	0.9830 g.	433.3 g.
III	66.00 g.	1.1173 g. 1.1142 g.	1.1157 g.	36.8 g.
IV	16.95 g.	1.1279 g. 1.1270 g.	1.1274 g.	9.6 g.
V-XII	75.40 g.	1.0247 g. 1.0277 g.	1.0262 g.	38.7 g.
XIII	<u>17.28 g.</u> 1433.78 grams	0.9400 g.	0.9400 g.	<u>8.1 g.</u> 706.3 grams

Summary.

Method of Extraction.	Wt. oxide extracted per 100 grams mona- zite residue.
Analysis by Hillebrand's method	39.40 g.
Analysis by modified method (1)	39.44 g.
(2)	39.30 g.
Digestion 2 g. residue with conc. $\text{HNO}_3$ (1)	15.73 g.
(2)	11.26 g.
Digestion 2 g. residue with conc. $\text{HCl}$ (1)	29.07 g.
(2)	25.35 g.
Digestion 2 g. residue with conc. $\text{H}_2\text{SO}_4$ (1)	39.87 g.
(2)	34.35 g.
Digestion 2 g. residue with conc. $\text{NaOH}$ (1)	38.89 g.
(2)	37.98 g.
Fusion 2 g. residue with $\text{Na}_2\text{CO}_3$ (1)	29.76 g.
(2)	30.77 g.
Fusion 2 g. residue with $\text{NaOH}$ and	
(1) Digestion oxide with dil. $\text{HNO}_3$ - 18.05 grams	
Digestion above residue with conc. $\text{HNO}_3$	- 14.40 " -32.45 g.
(2) Digestion oxide with conc. $\text{HNO}_3$ - 29.90 "	
Digestion above residue with conc. $\text{HNO}_3$	- 6.41 " -36.31 g.
(3) Digestion oxide with dil. $\text{H}_2\text{SO}_4$ - 24.74 "	
Digestion above residue with conc. $\text{H}_2\text{SO}_4$	- 9.08 " -33.82 g.
(4) Digestion oxide with conc. $\text{H}_2\text{SO}_4$ - 25.61 "	
Digestion above residue with water	- 11.52 "
Digestion above residue with conc. $\text{H}_2\text{SO}_4$	- 1.93 " -39.06 g.



Extraction per 100 grams monazite residue  
of

	Oxalate	Oxide
Digestion 1483 g. residue with NaOH	36.68 g.	18.34 g.
Fusion 872 g. residue with Na <sub>2</sub> CO <sub>3</sub>	66.51 g.	
Fusion 2000 g. residue with Na <sub>2</sub> CO <sub>3</sub>	71.69 g.	35.32 g.

The values obtained in the present investigation clearly show that fusion with sodium carbonate is the most efficient method of extraction of rare earths from sulphate residues. This method is not only most efficient but is also quite inexpensive, sodium carbonate and sulphuric acid being two of our cheapest chemicals. Since monazite residues are the source of nearly all cerium group rare earth elements, this research has uncovered a method of extraction that should be of great value to all workers in this field.

The above research was suggested by Dr. J. Allen Harris and carried out under his direction. I take this opportunity of thanking Dr. Harris for the great personal interest he has shown in the progress of this investigation.

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