DAEHAN HWAHAK HWOEJEE
(*Journal of the Korean Chemical Society*)
Vol. 23, No. 3, 1979
Printed in Republic of Korea

모나자이트의 분해

河 英 龜

서울대학교 자연과학대학 화학과

(1979. 1. 4 접수)

Decomposition of Monazite Sand

Young Gu Ha

Department of Chemistry, College of Natural Sciences,
Seoul National University, Seoul, Korea

(Received Jan. 4, 1979)

요 약. 이온교환법에 의하여 토륨과 희토류들을 분리해 내기에 알맞은 용액을 얻기 위하여 모나자이트를 황산으로 분해하였다. 황산분해는 모나자이트를 2.0시간동안 150~250 °C 온도에서 95 % 황산으로 분해시켰다.

황산과 모래의 무게비는 1:1.9~2.8로 실험하였으며 95 % 황산을 사용했을 때 200±5 °C 온도에서 2.0시간 처리하는 것이 가장 좋은 결과를 얻었으며 분해율은 99 % 를 넘는 것으로 밝혀졌다.

ABSTRACT. The purpose of this investigation was to study the sulfuric acid digestion of monazite sand, and to prepare rare-earths-thorium containg material from the resulting solution which would be suitable for further preparation of thorium and rare earth elements by ion-exchange. Digestion of crude monazite sand was treated in 95 % sulfuric acid for 2.0 hours at 150~250 °C. The acid to sand weight ratio were 1: 1.9~2.8. Optimum condition was 95 % sulfuric acid for 2.0 hours at 200±5 °C. Within this conditions monazite sand was decomposed up to 99 %.

INTRODUCTION

After world war II, many efforts has been expended by several research teams to develop an economic process for recovering thorium, rare earths and uranium from monazite sands. Moreover because its demand is highly increased recently, the production of rare earths for commercial uses have already reached to the magnitude of a large.

The monazite sands are an important source of the rare earths, they are chiefly separated from monazite sand. Monazite is essentially the orthophosphate of the rare earth elements of low atomic weight. This mineral occurs as a dense brown sand in some gravel beds and is particularly rich in the light rare earths of the cerium sub-group. The rare earth phosphates comprise about 80 to 95 percent of the total weight. Depending on the source, the thorium content varies from 6 to 10 percent. Uranium is present in monazite sands, its content varies from 0.2 to 1.0 percent. Typical analysis for monazite sands from various source-

are given in *Table* 1.

Due to the recent recognition of the rare earths and thorium as a decolorizer in the manufacture of glass, silica free optical glass, strong permanent magnet. color television and a potential reaction fuel, the atomic energy commision U. S. A. started research program to develop a process for producing pure rare earths and thorium from monazite sand.

Mainly two different process have been developed for chemically decomposing the monazite sands. Previous works the process were studied by Ames Laboratory Group and Battelle Memorial Institute. Battelle Memorial Institute[1] developed a process which involving digesting the monazite sands with caustic Soda. Ames Laboratory[2] based this process on the more commonly used sulfuric acid method of digestion[3].

The purpose of this investigation was to study the sulfuric acid digestion of monazite sand to prepare a thorium-rare earths containing material from the resulting solution which would be suitable for further separation by ion-exchange methods. It was also desired that the by-product uranium be recovered in a convenient form for further process.

Table 1. Composition of monazite sand.[a]

Constituent	Brazilian %	Indian %	S. African %	Jung-up[b] %
ThO_2	6.5	9.8	5.9	5.47
U_3O_8	0.17	0.29	0.12	0.34[c]
R_2O_3	59.2	58.6	45.2	65.[c]
Ce_2O_3	26.8	27.2	23.7	24.7
P_2O_5	26.0	30.1	27.0	—
Fe_2O_3	0.51	0.80	4.5	0.35
TiO_2	1.75	0.40	0.45	0.19
SiO_2	2.2	1.7	3.3	4.08

[a]John J. Braghusen, "Processing of Monazite Sands", ISC-947, 1957.
[b]B. C. Park and J. K. Lee, "Monazite Placer of Republic of Korea", , 1968.
[c]Y. G. Ha. unpublished data.

Studies were made in the laboratory to determine the optimum condition for the digestion of monazite sand and for the separation of thorium, rare earths and uranium by ion-exchange separation of monazite sulfate solution.

Mechanism of digestion of monazite sand in sulfuric acid, according to Fernelus[4], the reaction between sulfuric acid and monazite sand may be represented by the following equations:

$$2RPO_4+3H_2SO_4 \longrightarrow R_2(SO_4)_3+2H_3PO_4$$
$$Th_3(PO_4)_4+6H_2SO_4 \longrightarrow 3Th(SO_4)_2+4H_3PO_4$$
$$SiO_2\cdot xH_2+H_2SO_4 \longrightarrow SiO_2+H_2SO_4\cdot xH_2O$$

Where R symbolizes the rare earths.

EXPERIMENTAL AND RESULTS

The Screen Analysis and Magnetic Separation of Ground Jung-up Monazite. Jung-up (Korea) monazite sand was used in this study. For all sulfuric acid digestion, the screen analysis of ground sand magnetic separation were tested. The screen analysis of ground sand is shown in *Table* 2. and also is compared foreign monazite sand.

In this study, particle size distribution was

Table 2. The screen analysis of ground Jung-up monazite sand.

Mesh size		Jung-up wt%	Indian* wt%	Brazilian* wt%	Idoho* wt%
−28,	+35		—	2.5	2.3
	+40	1.2			
−35,	+50	9.0	0.07	11.9	18.4
−50,	+60	17.7	2.9	42.9	47.7
−60,	+80	27.4	—	—	—
−65,	+100	—	30.4	38.8	28.3
−80,	+100	22.4	—	—	—
−100,	+120	6.8	—	—	—
−120,	—	15.5	—	—	—
−100,	+150	—	54.0	35.5	2.8
−150,	+200	—	12.3	0.3	0.2

*Kernal Glenn Shaw, Ph. D Thesis, Iowa State Univ. (1953).

determined by a screen analysis of each of the two samples using eight inch Tyler Standard Screens (U. S. Standard Sieve Series, Fisher Scientific Co., Pittsburgh, Pa. U. S. A.) ranging from 40 mesh to 120 mesh. Up to the plus 20 mesh fraction contained large amounts of foreign material and do not contain very much monazite sand. There was also a considrable amount of gangue in the lower 100 mesh, as can be seen from the *Table* 2. These results are consistent with the fact that Korean Monazite Sand is similar to Brazilian and American monazite sand.

The results of magnetic separation of ground Jung-up monazite sand is shown in *Table* 3. and 4. In this study, Frantz isodynamic magnetic separator Model L-I was used.

Decomposition of Monazite Sand with Sulfuric Acid. The main objective of the laboratory studies were; first, to study the digestion of the monazite sand in order to lower the acid requirements and to determine the conditions necessary to make a pilot plant digestion; secondly, to develop a more direct method of preparing a rare earths-thorium containing material suitable for separation of rare earths by ion-exchange method.

Table 3. Magnetic separation of ground Jung-up monazite sand.

Mesh	Ilmenite wt%	Manazite Sand + Sand wt%	Monazite wt%	Sand wt%
−30, +40	26.0	74.0	95.4	4.6
−40, +50	19.8	80.2	96.0	4.0
−50, +60	13.6	86.4	91.6	8.4
−60, +80	8.7	91.3	86.3	13.7
−80, +100	5.7	94.3	82.2	17.8
−100, +120	3.6	96.4	76.6	23.4
−120 —	2.6	97.4	82.2	17.8

Frantz Iso-Dynamic Separator Model L-1

Table 4. R_2O_3 in monazite sand.

Mesh	R_2O_3 (%)
−40, +50	66.51
−50, +60	65.37
−60, +80	64.71
−80, +100	69.46

About 2 kgs of Jung-up monazite sand were prepred from screen analysis and magnetic separation, containing approximately −50 to +100 mesh size monazite.

The reaction between monazite sand and a mineral acid may be regarded as an erosion or corrosion process, proceeding at a rate which is dependent upon the mineral acid used, the temperature and concentration of the acid and surface characteristics of the sand particles. When sulfuric acid is used the fact that the products of the digestion were insoluble and form a coating over the surface of the monazite sand particles. The resistance of coating can be decreased by increasing the agitation. The acid requirements for the digestion of the monazite sand could be decreased by lowering the initial acid-to-sand ratio.

The lowest acid-to-sand ratio suggested throughly by Blickwedel[2] was 2.0 while complete digestion (up to 99 %) was not obtained at this ratio.

Optimum condition of acid-to-sand ratio was 2.8 in this studies. The results were shown in *Table* 5. when digesting only a few hundred grams of monazite sand in the laboratory scale the reaction was carried out in glass ware. However, in order of a pilot plant digestor to withstand the corrosive action of the hot sulfuric acid, so as to, we are recommend that it must be constructed of ceramic ware or glasslined steel.

Procedure. The sulfuric acid was reagent grade (Kanto Chemical Co., Inc., Japan) and this acid was assayed at 95 %. Oxalic acid was reagent grade (Kicita Chemical Co., Inc.,

Table 5. Decomposition ratio of sand with sulfuric acid (wt%).

Time (min)	150±5 °C		200±5 °C		250±5 °C	
	95% H_2SO_4(m*l*)					
	10.0	15.0	10.0	15.0	10.0	15.0
15			17.2	53.5		
20					76.6	89.1
30	33.1	35.3	33.3	75.2	79.3	89.7
40					79.9	89.8
45	36.9	40.6	39.8	78.9		
50					82.7	90.1
60	40.5	45.3	54.2	88.7	86.5	93.0
70					87.1	93.5
75	42.4	47.0	63.2	94.3		
80					89.2	96.3
90	42.8	47.8	69.3	97.0		
105	43.5	60.0	72.9	99.1		
120	47.1	62.0				
135	53.8	66.8				

*R_2O_3(%): 69.5

pan).

Weight out 10.0 g of monazite sand into 100 m*l* of porcelain dish or 100 m*l* of Pyrex evaporating dish and then added suitable amount of sulfuirc acid which is indicated *Table* 5. Put the porcelain dish on the electric hot plate previously adjust desired temperature. The mixture was occasionally stirred by means of a glass stirring rod, and the temperature was held at $x\pm5$ °C.

Decomposed mixtures were treated with 70 m*l* of demineralized water after cooling at room temperature, and the were digested for 1 hour. After digesting, the mixture solution were transfered into 250 m*l* of measuring flask and fill up with demineralized water to the mark. Shaking vigorously, stand it overnight to sediment undecomposed sand.

20.0 m*l* of aliquots were taken with pipett into the 100 m*l* beakers from the upper clean solution and added 20 m*l* of saturated oxalic acid solution to the beakers while stirring vigorously. For completly precipitation of rare earths and thorium, it must be stand overnight.

Filter off precipitates in the beakers using filter paper (Toyo Filter Paper No. 5B) and then wash the residure and the paper with deminerlized wate. Drying in the Electric Oven, and ignite the precipitates to constant weight. The results are shown in *Table* 5.

DISCUSSION

The reaction between the sulfuric acid and the sand was initiated by heating the samples to the desired temperature in the reaction poreclain dish. Agitation was continued until the reaction mixture was near solidification. The unreacted monazite sand was separated from the soltion by filteration. Shaw[3] recommended that a small quantity of very finely divided solid was also present in the solution. The major constituent of these solid was silica. The radiation survey shows that they contained a very large fraction of the radioactive daughter products of thorium

and uranium and that care should be taken in handling the solid.

The results of this study are shown in *Table* 3 and 5. Expect the rate of reaction is dependent not only on the rate of erosion, but also on the resistance of the insoluble coating to the transfer of acid to the surface of the particles. From this point on the reaction proceeds, we would like to recommend that monazite sand should be treated with screen and magnetic separator.

As can be seen from *Table* 5, the reaction between monazite sand and sulfuric acid meight be regarded as an erosion, proceeding at the rate which is dependent upon the sulfuric acid used, temperature and the sand particles. In accordance with these results, optimum condition was 95 % sulfuric acid for 2.0 hours at 200±5 °C.

ACKNOWLEDGEMENT

Th author gratefully acknowledge to the Korean Scientific Foundation for the financial support. The author wishes to express an appreciation to Mr. Jin Oh Kim for his assistance in the decomposition of monazite sand with sulfuric acid of this work.

REFERENCES

1. C. D. Colkins and R. B. Filbert, U. S. Atomic Energy Commission, BMI-244.
2. T. W. Blickwedel, U. S. Atomic Energy Commission, ISC-66.
3. K. G. Shaw, H. Smutz and G. L. Bridger, U. S. Atomic Energy Commission, ISC-407.
4. W. C. Fernelius, "Inorg anic Synthesis", Vol. III, New York. McGrow-Hill Book Co., Inc., 1964.