

INVESTIGATE DECOMPOSITION OF DONG PAO BASTNASITE WITH SULFURIC AT PILOT SCALE

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Abstract

To investigate effects of decomposition roasting temperature and necessary acid amount for decomposition, ore concentrate with TREO content about 39% was used as original ore concentrate (three samples named as Q3, Q5 and Q6), the rates of ore and acid (by chemical equivalence) were 1/1.6, 1/1.4 and 1/1.2, decomposition roasting temperatures were changed in a range of 400 – 420 °C, roasting time was 2h. During process of ore roasting decomposition, samples were taken out at different roasting temperatures. After that, these samples were dissolved by water at room temperature. Leaching then was filtered and the prepared solutions were kept and analyzed ICP to determine element concentrations

Key words: Bastnasite, Rare earths, decomposition, sulphation

ĐÁNH GIÁ KHẢ NĂNG PHÂN HỦY QUẶNG BASTNASITE DONG PAO VỚI AXIT SUNPHURIC QUY MÔ PILOT

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Tóm tắt

Để đánh giá ảnh hưởng của nhiệt độ phân hủy và lượng axit cần thiết cho phân hủy quặng bastnasit, tinh quặng với hàm lượng TREO 39% được nung phân hủy với axit sunphuric (ba mẫu Q3, Q5 và Q6), tỷ lệ quặng và axit (tương đương hóa học) là 1 / 1.6, 1 / 1.4 và 1 / 1.2, nhiệt độ nung phân hủy đã thay đổi trong khoảng 400 - 420°C, thời gian nung là 2h. Trong quá trình phân hủy quặng, các mẫu được lấy ra ở các nhiệt độ khác nhau. Sau đó, các mẫu này được hòa tan bằng nước ở nhiệt độ phòng, lọc và các dung dịch thu được phân tích ICP để xác định nồng độ nguyên tố, và đánh giá hiệu suất nung phân hủy.

1. Introduction

Rare earth metals and their compounds are in demand, and are often crucial for, a broad and rapidly expanding range of applications that rely upon their chemical, catalytic, electrical, magnetic, and optical properties. Rare earths are widely used for traditional sectors including metallurgy, petroleum, textiles, and agriculture. As indicated in [1], they are also becoming uniquely indispensable and critical in many high-tech industries such as hybrid cars, wind turbines, and compact fluorescent lights, flat screen televisions, mobile phones, disc drives, and defense technologies [2]. The widely method decomposition rare earth processing of bastnasite ore is sulfuric acid decomposition [3-9] because of getting large quantity of product. The mixing ore and acid was headed to 300 to 400 °C after that leaching to get rare earth sulfate

solution. However, this method releases to toxic gases HF and SO_x so the gases were treated by absorber.

2. Experimental

2.1 Chemical and equipments

a. Chemical:

The Dong Pao ore concentrate was enriched by flotation at Institute for Technology and Rare Elements with concentrate 39% of total rare earth oxide. The chemical such as sulfuric is industrial chemical, from Vietnam.

b. Equipments:

The rotary furnace and absorber system was supported by Japan with characterizations, capacity 50 kg ore per batch, using LPG gas as a heat source, max temperature 850 °C. The sample in furnace can be taken out at any temperature rang. Analytical equipments to estimating the decomposition process such as;

XRD Brucker D8-Advance (Germany), HSEM JOEL (Japan), ICP-OES Ultima 2-Horiba (Japan).

2.2. Experiment carried out

50 kg of ore was mixed with sulfuric acid at different ratio at a mixer in 2 hr after that the mixing ore and acid was added into rotary furnace then roasting. The roasted sample was taken out at different roasting temperature to determine the yield of rare earth.

3. Results and discussion

3.1. Characterization of ore concentrate

In order to determine physical properties of ore concentrate, ore was grinded. Ore grain dimension was characterized by laser diffraction method that has been shown in Figure 1. Ore grain morphology was characterized by SEM as in Figure 2. Mineral content of ore concentrate was determined by XRD as in Figure 3. And chemical content of ore concentrate was determined by ICP as in Table 1. As shown in Figure 1, the mean size of ore grain was about 15 μm . Figure 3 indicated that mineral content in Dong Pao ore concentrate was almost bastnasite, a little content of synchysite and barite.

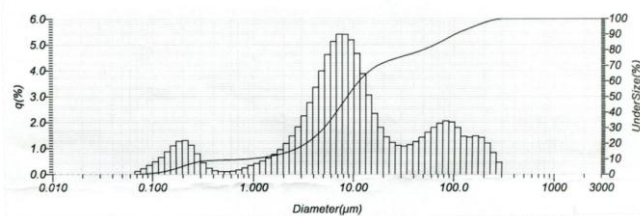


Figure 1. Laser diffraction spectrum of ore concentrate.

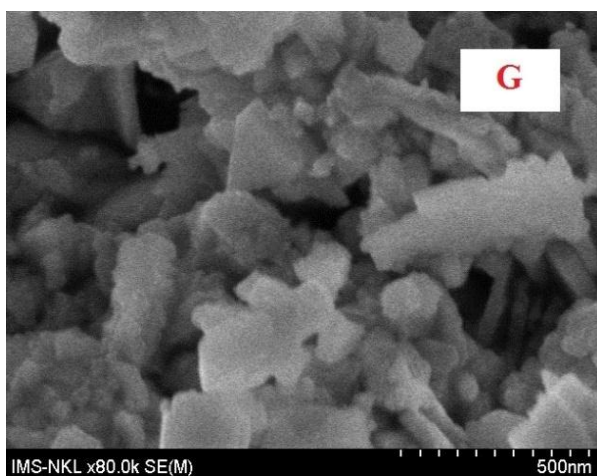


Figure 2. SEM image of ore concentrate.

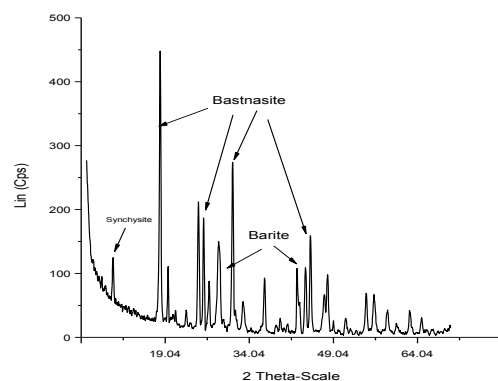


Figure 3. XRD spectrum of ore concentrate.

Table 1: RE and impurities concentration of original ore concentrate of samples Q3, Q5 and Q6

Element	Unit	Samples		
		Qo.3	Qo.5	Qo.6
Y	mg/kg	972.7	915.9	855.6
La	mg/kg	127200	126142	127876
Ce	mg/kg	149619	152122	151671
Pr	mg/kg	12531.3	12227.6	12348.4
Nd	mg/kg	33036.5	32067.6	32556.1
Sm	mg/kg	1907.9	1850.6	1863.8
Eu	mg/kg	392.5	370.6	340.5
Gd	mg/kg	905.6	865.9	775.4
Tb	mg/kg	67.5	62.6	63.2
Dy	mg/kg	134.3	128.5	133.1
TREO	%	39.2	39.2	39.4
Ca	mg/kg	11373.2	11868.5	10650.3
Fe	mg/kg	6347.6	6195.5	5292.6
Mn	mg/kg	3401.3	2932.8	2566.4
Al	mg/kg	1522.5	1244	3512.2
Mg	mg/kg	507.5	638.9	393.4
Pb	mg/kg	860.8	894	775.5
Si	mg/kg	1518.6	1401.6	1569.4
Zn	mg/kg	61.6	63	57.6
Th	mg/kg	131.3	128.7	125.9
U	mg/kg	119.1	99.8	106.8

The mineral content of three original ore samples Q3, Q5, and Q6 has been shown in Table 1 showed that these samples have quite

similar mineral contents. Three samples were mixed with sulfuric acid with different ore/acid rates to study effect of acid amount on RE recover yield.

3.2. Decomposition of bastnasite ore with sulfuric acid

Figure 4. Process of mixing, roasting ore with acid at pilot scale.

Images in Figure 5, Figure 6 and Figure 7 showed that with high acid amount, mixture after mixing was wet and stucked on the wall of mixing machine (as Figure 5). When reducing acid amount, mixture after mixing became drier and made small grains that were not stucked on the wall of mixing machine. Therefore, with low acid amount, it would be easier for mixing and the mixture after mixing was not stucked on the wall of furnace Table 2 showed that although used acid weight of sample Q3 was higher than that of sample Q5, total weight of mixture after mixing of Q3 taken out of machine was lower than that of Q5 taken out of machine. The reason for this is that with high acid amount, mixture was stucked on the wall, causing difficulties in taking out mixture after mixing. With drier mixture because of lower acid amount, it would be easier to take out mixture. With ore/acid rate of 1/1.2, mixture weight was lowest because of the lowest acid weight.



Figure 5. After mixing ore and sulfuric acid with ore/acid rate = 1/1.6 (Q3).



Figure 6. After mixing ore and sulfuric acid with ore/acid rate = 1/1.4 (Q5).



Figure 7. After mixing ore and sulfuric acid with ore/acid rate = 1/1.2 (Q6).

Table 2: Parameters for mixing process and weight of mixture after mixing

Condition	Q3 sample	Q5 sample	Q6 sample
Weight of ore concentrate (kg)	50	50	50
Weight of H ₂ SO ₄ 98% (kg)	33	28.7	25

Ore conc/acid(weight ratio)	1/0.66	1/0.574	1/0.5
Theoretical ore conc/acid ratio	160%	140%	120%
Time of adding H ₂ SO ₄	30 minutes	30 minutes	30 minutes
Cooling time (room temp)	30 minutes	30 minutes	30 minutes
Mixing time	60 minutes	60 minutes	60 minutes
Weight of mixture after mixing	72.2 kg	72.8 kg	67.3 kg

During roasting, sample temperature was checked by using thermal sensor. A little amount of sample has been taken out to determine effect of decomposition roasting yield on roasting temperature. Taking out samples for analysis was carried out since sample temperature reached 200 °C. Samples at different roasting temperatures were leached by water. The leaching was analyzed ICP to detect RE and impurity concentrations. The residues after leaching continue to disintegrated to determine the rest of RE and impurity concentration. Based on results of ICP and residue analysis, RE decomposition yield at different roasting temperatures would be calculated. From this calculation, it can be seen that which roasting temperature would give the best RE recover yield and how much impurities were co-existed.

Figure 8, 9, 10 showed the color of roasted samples. At low roasting temperature, the color of roasted ore was white. At higher roasting temperatures, the color of roasted ores changed gradually to red. The reason of this is that at high roasting temperature, Fe₂(SO₄)₃ was disintegrated to Fe₂O₃ that is red. In other word, at this roasting temperature, ore was disintegrated completely. Therefore, based on roasted ore color, it can be known that if ore decomposition finishes or not.



Figure 8. The colours of roasted ore Q3 at different roasting temperatures.



Figure 9. The colours of roasted ore Q5 at different roasting temperatures.



Figure 10. The colors of roasted ore Q6 at different roasting temperatures.

Table 3: Weight of original ore, after-mixing ore and after-roasting ore

Sample	Q3	Q5	Q6
Weight of ore concentrate (kg)	50	50	50
Weight of H ₂ SO ₄ 98% (kg)	33	28.7	25
Mixed weight (kg)	72.2	72.8	67.3
Roasted weight (kg)	56.05	56.85	55.8

The weight of ore after roasting of Q3 and Q5 was almost same, about 77% weight of ore after mixing. With Q6, weight of ore after roasting was about 83% weight of ore after mixing. Therefore, after roasting process, mixture of ore concentrate and sulfuric acid with low acid amount gained higher weight rate. However, the weights of after-roasting ore of 3 samples Q3, Q5, Q6 were almost same. It can be said that during roasting decomposition, weight of after-roasting ore was changed insignificantly although weights of mixtures for mixing were different. If excess acid amount was high, during roasting process, excess acid would be decomposed keeping an almost no-changed weight after roasting (Table 3). This means that after-roasting ore weight just depends on weight of initial ore concentrate.

The weights of after-roasting mixture with sample Q3 and Q5 were almost similar to each

other, about 77% weight of after-mixing mixture. With Q6, weight of after-roasting mixture was about 83% weight of after-mixing mixture. Therefore, after roasting process, the ore mixture with low acid amount reached higher weight rate.

The results of leaching process of samples taken out from different roasting temperatures with Q3, Q5, Q6 have been shown in Table 4, 5 and 6. The samples taken out from different temperatures were leached by water with solid/liquid rate of 1/10. 5 g sample was grinded, and then leached by 50 mL H₂O. Filter to collect leaching solution, check pH of leaching, and add H₂O to 100mL, then analyze ICP to detect RE and impurity concentrations. The residue was dried, then disintegrated to determine RE and impurity concentrations in the residue.

Table 4: The results of leaching of samples taken out from different roasting temperatures of original sample Q3

Elements	Unit	Roasting temperature (°C)					
		190	260	410	415	455	Final*
Y	mg/l	45.6	53.2	55.4	57	55.2	55.4
La	mg/l	8221.8	8921.4	9546.8	9762.6	9371.6	9185
Ce	mg/l	8411.4	10829.2	11563.4	11648	11130.6	10580.4
Pr	mg/l	785	825.8	969	976.2	930.6	932
Nd	mg/l	2000.8	2057.8	2404.6	2343.4	2286.4	2335.8
Sm	mg/l	179.6	196	206.2	215.4	206.8	199.2
Eu	mg/l	28.2	32.8	33.6	34.2	33	32.2
Gd	mg/l	62.2	70.8	73.6	73.2	74.2	72.6
Tb	mg/l	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Dy	mg/l	10.2	11.4	11.8	12	12.2	12
Ho	mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Er	mg/l	3.8	2.2	2.2	2.2	1.6	1.6
Tm	mg/l	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Yb	mg/l	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17
Lu	mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
REEs	g/l	19.8	23	24.8	25.2	24.2	23.4
U	mg/l	8.2	8	7.8	8	7.8	8.2
Th	mg/l	11.6	8.4	7	4.4	0.8	0.6
Ba	mg/l	2	<0.5	<0.5	<0.5	<0.5	<0.5
Mg	mg/l	21.6	18	16.8	18	24.6	20.2
Pb	mg/l	25.8	15.8	13.2	13.8	10	10.4
Si	mg/l	5.6	7	6.6	6.6	6.4	6.2
Zn	mg/l	10.2	8.6	8.4	10	12.2	11.2
Al	mg/l	430.8	364.4	327.8	329.6	194.4	190.6
Ca	mg/l	512.4	575.4	611.2	573.8	682	552.2
Fe	mg/l	326.8	182.2	154	97	13	5.4
K	mg/l	193	202.8	213.8	251	258.4	230.6

Mn	mg/l	137.8	172	171.2	210.4	295	348.6
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* *Finishing roasting*

Table 5: The results of leaching of samples taken out from different roasting temperatures of original sample Q5

Element	Unit	Roasting temperature (°C)					
		200	310	325	400	420	Final
Y	mg/l	37.8	50.4	49.8	50.4	47.8	54
La	mg/l	6828.8	8710.2	9254.2	9137.6	8792.2	9825
Ce	mg/l	6693.8	8021.8	10764.6	10503.4	10220	11718.4
Pr	mg/l	669.2	852.4	920	941.6	881	980.8
Nd	mg/l	1632.2	2147.6	2305	2276.8	2200.6	2403
Sm	mg/l	158.6	186.6	199.6	205.2	187.4	209.2
Eu	mg/l	22.4	30.4	30.6	31	29.2	32.6
Gd	mg/l	49.2	63.4	66.6	68.2	65.6	71.6
Tb	mg/l	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Dy	mg/l	8.2	10.6	11.2	11.2	10.8	11.8
Ho	mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Er	mg/l	3	3.8	2.2	1.6	2.2	2.2
Tm	mg/l	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Yb	mg/l	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17
Lu	mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
REEs	g/l	16.2	20	23.6	23.2	22.4	25.4
U	mg/l	7.4	8	7.4	7	7.2	8
Th	mg/l	9	10	9.6	8.8	7.8	6.4
Ba	mg/l	2.8	<0.5	<0.5	<0.5	<0.5	<0.5
Mg	mg/l	12.2	17.6	18.4	13.8	12.6	14.2
Pb	mg/l	20.2	27.6	22	11.4	9.8	9
Si	mg/l	4.2	5.6	6.2	6.2	4.8	6.2
Zn	mg/l	7	10.2	9.8	9.8	8.8	10.2
Al	mg/l	260	298.4	318.6	222.8	204.8	166
Ca	mg/l	472.6	567.6	574.4	611.6	474.2	542
Fe	mg/l	372.8	333.6	274	105	15	6.7
K	mg/l	209.2	247.4	280.4	278.2	232.8	241.4
Mn	mg/l	162	156	208.2	250.8	255.8	269

Table 6: The results of leaching of samples taken out from different roasting temperatures of original sample Q6

Element	Unit	Roasting temperature (°C)						
		208	267	297	350	380	385	Final
Y	mg/l	41.6	46.8	57.2	12.6	48	48.2	52.8
La	mg/l	7255	8417.8	9440.2	8809.6	8640.4	8362.4	9741
Ce	mg/l	6316	8670.6	11141.4	10301.6	9652.8	9467.2	10827.2
Pr	mg/l	732	844	983.4	898.8	867.6	838	983.2
Nd	mg/l	1849.4	2062.8	2401.2	2259.4	2160.8	2145.6	2401.6
Sm	mg/l	169.2	183.4	210.4	201.4	189.4	187	205.4
Eu	mg/l	24.8	28	32.6	29.8	28.6	28.2	32.4
Gd	mg/l	52.2	60.6	72	65.4	64.6	64.2	70.6
Tb	mg/l	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09	<0.09
Dy	mg/l	9.2	10.4	12	11	10.6	10.4	11.6

Ho	mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Er	mg/l	3	3	3	1.6	1.6	1.6	1.6
Tm	mg/l	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12	<0.12
Yb	mg/l	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17	<0.17
Lu	mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
REEs	g/l	16.4	20.4	24.4	22.6	21.6	21.2	24.4
U	mg/l	9.2	8.8	9.4	5.2	8	7.8	7.2
Th	mg/l	9.2	9.6	10.2	5.6	1	1	0.8
Ba	mg/l	1.6	2.4	1.4	<0.5	0.5	<0.5	<0.5
Mg	mg/l	19.2	18.6	25.6	24.8	25.8	24.8	25.2
Pb	mg/l	18.4	14.8	11.8	8.6	8.6	7.8	10.4
Si	mg/l	4.8	4.6	7.4	5.2	6	5.8	5.8
Zn	mg/l	10	9.8	11.8	13.6	12.4	12.4	11.6
Al	mg/l	387.4	301.6	469	165.8	111	102.8	144.2
Ca	mg/l	421.6	460	546.2	513.2	498.6	513.6	513
Fe	mg/l	350.4	319.6	318.4	64.4	9.2	8.2	5.6
K	mg/l	208.6	182.6	241.4	213.4	219	215.6	250.6
Mn	mg/l	136.2	175.4	289.6	350.6	347.8	358	325

5. Conclusions

Investigation of mixing acid and ore concentrate with different ore/acid rate has been carried out in this work. The results indicated that it was possible to reduce sulfuric acid amount and still remain high RE recover yield. With ore/acid rate of 1/1.2, RE recover yield was 94%. However, to assure high RE recover yield, it is necessary to increase ore/acid rate up to 1/1.3.

With the roasting temperature of sample of 400 °C for a time of 1.5 – 2h, RE recover yield reached highest. Increasing roasting temperature caused decreasing RE recover yield and lead to an unnecessary energy cost.

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