Nucl. Sci. and Tech., Vol.8, No. 2 (2018), pp. 36-42

Nuclear Science and Technology

Journal homepage: https://jnst.vn/index.php/nst

Studying digestion conditions of Vietnamese monazite with acid sulfuric for the recovery of rare earth elements, thorium and uranium

Nguyen Van Tung, Nguyen Van Phu, Nguyen Phuong Thoa, Tran Hoang Mai, Luu Xuan Dinh

Institute for Technology of Radioactive and Rare Elements, 48 Lang Ha Str, Dong Da Dist, Hanoi
Email: lxdinh79@gmail.com

Abstract: The monazite ore is a commercial source of Th, U and rare earth in Vietnam. There are two methods, which were often applied to decompose monazite ore are alkaline and sulfuric methods. But in Vietnam, sulfuric method is more suitable due to the simple technology. In sulfuric acid treatment its breakdown using sulfate process for recovering of REEs, thorium and uranium. In this study, the parameters such as ore/acid ratios, the digestion temperature and the time of degestion were investigated to determine optimal digestion conditions for high recovery of main ingredients (REEs, Th, U) in monazite ore. The results shown that the optimal parameters for the digestion are ore/acid ratio 1.2:1, digestion temperature - 300ºC and time of digestion - 1 hour, the recoveries for REEs, Th and U are namely 90%, 85% and 65%, respectively.

Keywords: *monazite ore sulfates process, RE, Th and U.*

I. INTRODUCTION

In order to use effectively RE sources in Vietnam, monazite is a commercial source of Th, U and rare earth needed to be investigated and recovered completely. There are two methods which were often applied to decompose monazite ore are alkaline and sulfuric methods. In the process for the decomposition of monazite using alkaline, the ratio of caustic soda to monazite depends on the source, purity and particle size of the monazite ore concentrate. The temperature of the sodium hydroxide treatment should be maintained at 140°C to avoid the formation (of a portion) of hard refractory oxide and at the same time to maintain high breakdown efficiency. In other to improve efficiency, the monazite ores require grinding to the size of 300 meshes before digestion to obtain the high recovery of digestion process. The process was conducted at a temperature around 140ºC – 170ºC for 3-10 hours [1-2]. In the alkali treatment of monazite, both thorium and uranium would accompany rare earth elements. The result is formation of hydrous oxide cake**.** In the meantime some silica would react with the caustic soda forming a soluble sodium silicate**.** So it caused difficult for leaching and filtrating hydrous oxide cake by acid due silical-gel.

In the sulfuric acid treatment, the sulfate ion acts as the anion forming RE sulfate [3-5]. A major disadvantage of sulfuric acid processing is the loss of the phosphate, which may have potential economic value. However, sulfuric acid process does not yield pure products and is no longer in use [3] because it consists of Th and U. Both U and Th which are exist in their anionic complex forms namely $(Th(SO_4)_n)_{4-2n}$ and $(UO_2(SO_4)_{n2-2n})$ can be properly separated by Primene JM-T and Alamine 336 solvent extraction. Using

https://doi.org/10.53747/jnst.v8i2.89
Received 02 February 2018, accepted 24 Jun 2018

simultaneous solvent extraction of both Th and U could be achieved from the sulfate leach liquor up to 99.9 and 99.4%, respectively [6]. The monazite was reacted with concentrated sulfuric acid at temperature around 200°C-350°C until became to a solid state – roasted ore. This solid was dissolved in water. The resulting solution contains the thorium, the uranium and the rare earths. Thorium and uranium was then separated from rare earths by applying solvent extraction methods and rare earths were precipitated via double sulfate [7-10].

In this study, the parameters such as ore/acid ratios, the digestion temperature and time were investigated to determine optimal digestion conditions for high recovery of main ingredients (REEs, Th, U) in monazite ore.

II. EXPERIMENTS

A. Material

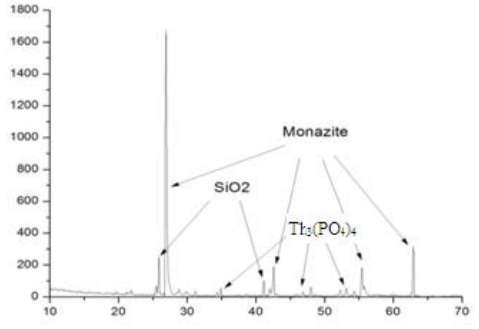

Fig.1. XRD patent of Vietnamese monazite ore

Table I. Chemical compositions of Vietnamese monazite ore

Elements	Content (%)
La	8.4
Ce	17.11
Pr	1.94
Nd	6.58
Sm	1.37
Eu	0.05
Gd	0.83
Tb	0.15
Dy	0.62
Tm	0.12
Er	0.27
Y	2.4
Ho	0.04
Yb	0.21
Lu	0.03
Th	3.87
U	0.16

Monazite concentrate was provided from Binh Thuan province, Viet Nam with density of 3 g/cm^3 and particle size of 1 mm. To determine the moisture content of the monazite concentrate, approximately 40 g of concentrate were carefully weighed and placed in a drying oven set at 80°C for several days. After the sample was allowed to cool, the weight of the sample was exactly the same as it was before drying. This shows that the monazite concentrate was completely free from moisture. X-ray diffraction (XRD) analysis (Brucker D8-Advance- Germany) was carried out on the monazite concentrate to determine the major mineral phases present (figure 1). The XRD results show that the major constituents of monazite ores are monazite-Ce, $Th_3(PO_4)_4$ and SiO_2. The mineral components of Vietnamese monazite are same with that of other monazite in the World [3-5]. Sulfuric acid (99% purity) was used in this study. Deionized (DI) water was used in water leaching experiments. The chemical contents of rare earth elements in monazite account for 40.11% in weight while Thorium is 3.87%. The results obtaining is showed in the Table I.

Rare earths exist mainly in a form of light rare earths (especially monazite-Ce). There is only 3.7% of Th which is equivalent

to 1/10 rare earths. The components of Vietnamese monazite compared with that of other monazites, for example Egyptian monazite, the rare earths and Th components are higher than that of Vietnamese monazite [4], but Th component in Vietnamese monazite is higher than that of Korean monazite [3]. So the rare earth component of monazite depended on how to beneficiation process, the Th content depends on the characteristic monazite deposition.

B. Method of experiments

Concentrated sulfuric acid was heated to reach the temperature at 180°C. Then, 50g of monazite ores were added with the different acid/ore ratios. The mixture of sulfuric acid and monazite were then digested at different temperatures and different times. Finally, the pasty mass obtaining from the decomposition process was treated with water (the pasty mass/H_2O ratio was 1/10) and a solution to take $RE_2(SO_4)_3$ away from acid-insoluble residue. U, Th, and rare earth elements concentrations of the leachate were measured by ICP-OES and determined the recovery of the decomposition process.

III. RESULTS AND DISCUSSION

A. Effect of the amount of sulfuric acid used in the decomposition process on the recovery

Heating concentrated sulfuric acid was carried out at 180°C, then, 50g of monazite ores was added with acid with different ore/acid ratios. The mixture of ore and acid were decomposed at 300°C for 2 hours.

Table II shows that, the recovery efficiency of middle groups such as Sm and Dy had better than that of the light rare earth elements at the 2 and 1.8 ore/acid ratios. Also at these ratios the recovery efficiency of Ce reached the lowest of 36.6 and 54.2%, respectively. As the ore/acid ratio decreases to the limit, the decomposition efficiency of the rare earth elements increases markedly. For example, at an ore/acid ratio of 1.2, the recovery efficiency of the rare earth elements was over 90%. The recovery efficiency of La, Ce, Nd and Pr was only 93,7; 87,8; 93,6 and 93,3%, respectively.

Table II. Influence of acid/ore ratio on the recovery of rare earth elements

Elements	Initial monazite ore	Ore/acid ratio (g/g)											
		2		1.8		1.6		1.4		1.2		1	
	mgkg	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%	mg/L	%
La	9827.46	4757.2	48.41	6449.0	65.62	6734.7	68.53	8306.1	84.52	9214.3	93.76	9367.3	95.32
Ce	19169.06	7028.9	36.67	10389.1	54.20	11984.4	62.52	14192.6	74.04	16838.5	87.84	15661.5	81.70
Nd	7688.81	3054.7	39.73	4309.7	56.05	4592.1	59.72	6302.5	81.97	7216.4	93.86	7688.1	100.00
Pr	2220.37	829.5	37.36	1179.8	53.14	1420.5	63.98	1640.7	73.89	2073.3	93.38	1923.6	86.63
Sm	1165.43	598.2	51.33	823.0	70.62	876.5	75.21	1062.3	91.15	1167.5	100,01	1083.7	92.99
Dy	499.47	334.7	67.01	388.4	77.76	436.3	87.35	486.1	97.32	500.0	100,00	492.8	98.66
Er	231.57	119.0	51.39	142.1	61.36	172.4	74.45	222.8	96.21	213.7	92.28	170.3	73.54
Y	2003.94	1464.5	73.08	1575.7	78.63	1816.7	90.66	2003.0	100,0	200,0	100.0	1956.6	97.64

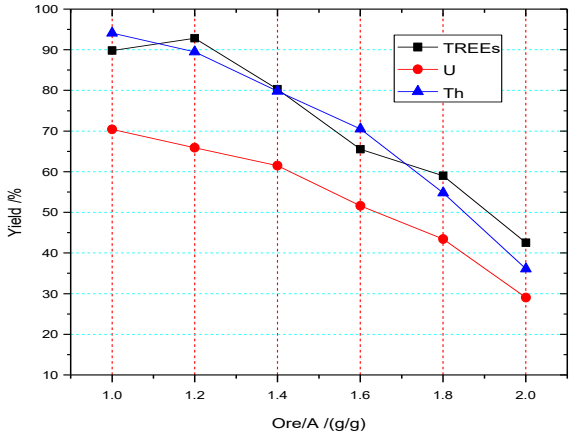

Fig. 2. Influence of ore/acid ratios on the recovery of TREEs (total rare earth elements), Th and U.

Figure 2 illustrated that effect of ore/acid ratios on the recovery TREEs (total rare earths), Th and U, at ratio ore/acid was 2/1 so, the recovery efficiency of TREEs and Th were very low. When decreasing the ratio the recovery efficiency of TREEs, Th increasing so much and reached to 90% at ratio 1/1, if increasing this ratio to 1.2/1 the recovery efficiency of TREEs and Th did not increase but the recovery efficiency of U decreased slowly from 70 to 65%. The best ratio ore/acid is 1.2/1, that used for studying further such as, time and temperature digestion.

B. Investigation for temperature and time on the decomposition process

The optimal ore/acid ratio of 1.2/1 was used to conduct the experiments of assessing interference of temperature and time on the decomposition process. The temperatures and times of the decomposition are given in the Figure 3. The temperatures in the decomposition process were changed from 200^{o}C to 450^{o}C and times were changed from 1 hour to 4 hours, The Figure 3 showed that the digestion time and temperature increased the sample color changed to light gray.

The roasted ores were leached with water with solid/liquid ratio 1:10, then filtration, the solution was determined by ICP-OES to calculate recovery of rare earths, Th and U. The Table III showed the recovery efficiency (%) of light rare earths of sample, which just mixed sulfuric acid with monazite at 180^{o}C the recovery efficiency of light rare earths reached to 75%. In other to improve the recovery the mixing sample was roasted at higher temperature and digestion time from 1 to 4 hrs.

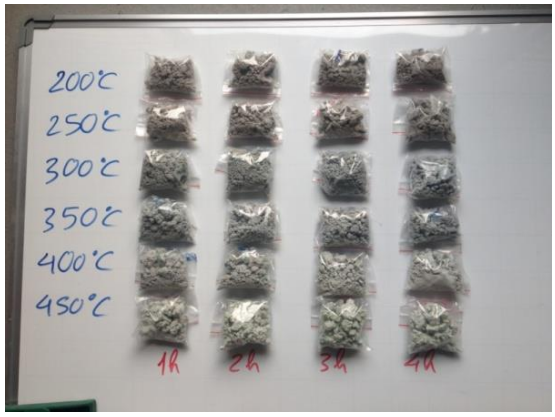

Fig. 3. Images of samples in different digestion temperatures and times

The results from Figure 4 showed that the highest recovery efficiency of rare earths is 96% at 300^{o}C for 4 hours. The recovery efficiency of rare earth elements increased gradually range from 200^{o}C to 300^{o}C according to the time. When the temperature of

the process was among from 300°C to 450°C, the recovery efficiency of rare earth elements decreases gradually according to the time and the digestion time is 1 hour, the recovery reached the highest values among these temperatures. For example, the recovery of rare earths was 92% at 350°C. When the time of the decomposition was increased to 4 hours, the recovery was only 77%. This phenomenon is interpreted that when the temperature is over 350°C or the time is longer than needed, rare earth salts became unable to dissolve into a solution.

Figure 5 was the dependence of temperature and time on the Th recovery efficiency. At digestion temperatures from 200 to 250°C, the recovery efficiency increases as the digestion time increases. The recovery of thorium was the highest (98%) at 250°C for 4 hours. When the digestion temperature over 250°C the recovery efficiency reduces so much and the longer the decomposition time, the lower efficiency, for example at 450°C for 4 hours the efficiency was only 20%.

Figure 6 is the recovery rate of U depending on the temperature and the heating time. It shows that when the temperature of the decomposition to above 400°C for 1 hour, the recovery efficiency of U is only 50%. When increasing the digestion time the efficiency decreases to less than 25%. When the digestion temperature below 400°C, the recovery efficiency is in the range of 50 to 70% depending on the digestion time. At digestion temperature of 350°C for 1 hour, the highest efficiency is 71%. However, when the digestion time increases, the efficiency decreases to 50% when heated for 3 hours.

As mention above with propose is getting highest recovery of rare earth, Th and U so the digestion condition at 300°C for 1 hour, the recoveries of rare earths, Th, U are 90%, 85% and 65% respectively. The advantages of these conditions are the temperature is not too high, and saving the time and energy so that they will be used to decompose monazite ores in lager scales.

Table III. Recovery of rare earth from sample mixing with acid at 180°C without digestion

Recovery	Elements					
	La	Ce	Pr	Nd	Sm	Y
%	75.17	70.90	76.93	78.80	67.97	57.61

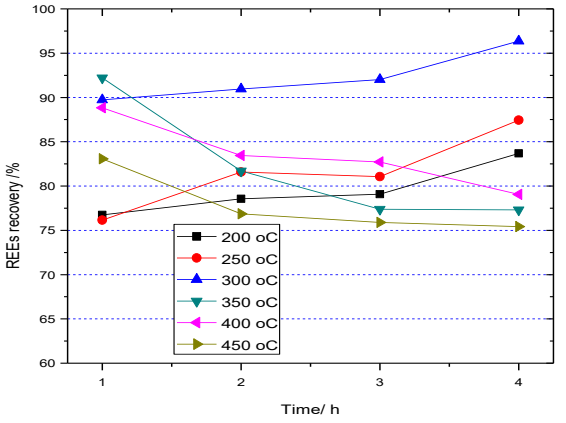

Fig. 4. Dependence of the total rare earth elements recovery on digestion temperatures and times

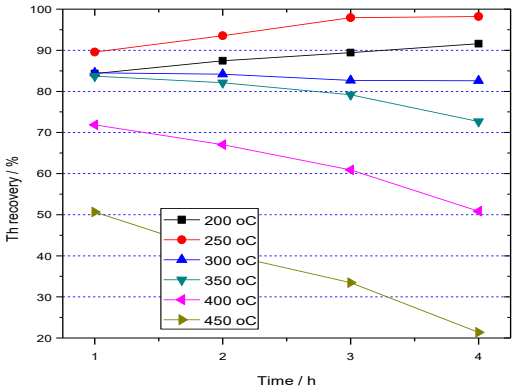

Fig. 5. Dependence of the Th recovery on digestion temperatures and times

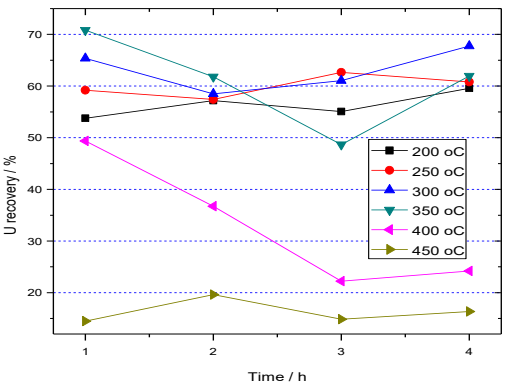

Fig. 6. Dependence of the U recovery on digestion temperatures and times

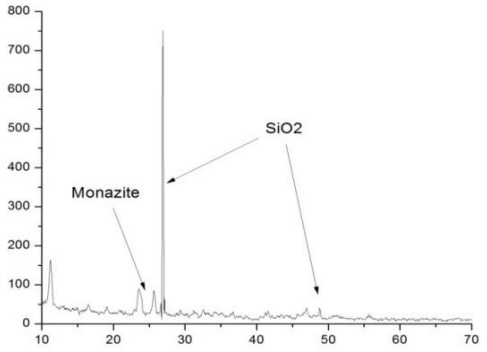

Fig. 7. XRD characterization of residue sample, decomposed at 300^{o}C and for 1h (M1).

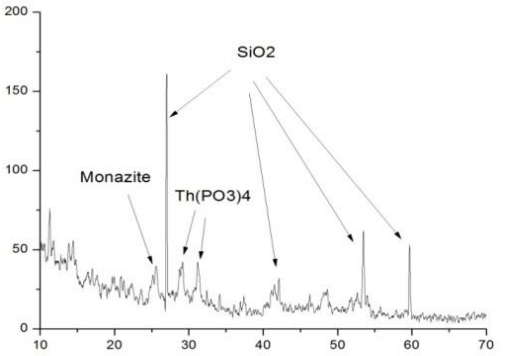

Fig. 8. XRD characterization of residue sample, decomposed at 450^{o}C and for 4h (M2).

The residues remaining from the leaching process of digestion temperature at 300^{o}C digestion 1h (named M1) and digestion temperature at 450^{o}C digestion 4h (named M2) samples were determined by XRD. The results were illustrated in Figure 7 and 8. The XRD patent of M1 showed that the residue consisted of small amount of monazite, that has not reacted and SiO_2 (Figure 7). For the residue of M2 sample showed that the components consisted of a little monazite, SiO_2 and $(ThPO_3)_4$. This thing could be explained that at high temperature, thorium in monazite ores was transferred into the thorium phosphonate which is difficult to dissolve in water, and it exists into the residue.

IV. CONCLUSIONS

In this study, were determined optimal digestion conditions for high recovery of main ingredients (REEs, Th, U) in monazite ore. The results showed, that the ore/acid ratio was 1.2/1, the digestion temperature at 300^{o}C for 1 hour, the recoveries for REEs, Th and U are namely 90%, 85% and 65% respectively.

REFERENCES

[1] Le Dang Anh, The trial production deployment of rare earth chloride from monazite ore Vietnam pilot line on aid India, the state project in 1993.

[2] L. Berry, J. Galvin, V. Agarwal, M.S. Safarzadeh, ‘*’Alkali pug bake process for the decomposition of monazite concentrates*’’ Minerals Engineering 109, pp 32–41, 2017.

[3] T.E. Amer, W.M. Abdella, G.M. Abdel-Wahab, E.M. El-Sheikh. ‘*’A suggested alternative procedure for processing of monazite mineral concentrate*. Int. J. Miner. Process. 125, 106–111, 2013.

[4] N.A. Abdelfattah, A.A. Abdou* and A.R, Bakry, ‘*’A novel Procedure for the Recovery of Rosetta Monazite Metal Values through its Acid Treatment*’’ Chem Sci Rev Lett, 4(13), pp 259-266, 2015.

[5] W. Xiuyan, L. Jiemin, L. Mei, F. Huili, and Y. Qishan, ‘’*Decomposition reaction kinetics of Baotou RE concentrate with concentrated sulfuric acid at low temperature*’’ *RARE METALS* Vol. 29, No. 2, p. 121, 2010.

[6] J.C.B.S. Amaral, C.A. Morais, “*Thorium and uranium extraction from rare earth elements in monazite sulfuric acid liquor through solvent extraction*”, Minerals Engineering, 23, pp. 498 – 503, 2010.

[7]K.A. Rabie, S.M. Abdel – Wahaab. *“Monazite – Uranium separation and purification applying oxalic – nitrate – TBP extraction”* Arab journal of Nuclear Science and Applications, 46(1), (30-42), 2013.

[8] C.J. Kim, J. R. Kumar, *“Solvent extraction studies on uranium using amine based extractants and recovery from low grade ore leach liquors”*, J. Braz, chem.Soc, Vol 23, No 7, 1254-1264, 2012.

[9] C.A. Sharrad, D.M. Whittaker, “*The use of organic extractants in solvent extraction processes in the partitioning of spent nuclear fuels”*, in Reprocessing and Recycling of Spent Nuclear Fuel(Issue). 153 – 189, 2015.

[10] A.M.I. Ali, Y.A. El-Nadi, J.A. Daoud, H.F. Aly, “*Recovery of thorium (IV) from leached monazite solutions using counter-current extraction”*, Int. J. Miner. Process. 81, 217–223, 2007.