



Investigation of Vietnamese monazite concentrate decomposition by alkaline (KOH) baking method

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Abstract: The alkaline (NaOH) hydrometallurgy for monazite concentrate is currently being used in the industrial production of total rare earth oxides (TREOs) and thorium oxide (ThO₂). Besides the acknowledged advantages, the hydrometallurgical process also has certain disadvantages such as the requirement of ultra-fine grinding to -325 mesh and the hydrometallurgy time extended from 8 to 10 hours to achieve ~93% efficiency. The present paper reports a new roasting process using potassium hydroxide (KOH) applied to Vietnamese monazite concentrates. The experimental data were collected using mass analysis, XRD, and ICP-OES analysis. The optimal efficiency of the process was ~95% after roasting time of 0.5 hours, the temperature at 250°C, and KOH:monazite mass ratio = 1:1. Thereby, the alkaline (KOH) roasting process solved limitations of the alkaline (NaOH) hydrometallurgy and showed the development potential in deep processing of the monazite concentrate.

Keywords: *Vietnamese monazite concentrate; alkaline (NaOH) baking; alkaline (KOH) baking process.*

I. INTRODUCTION

Many groups around the world have developed different industrial processing methods for monazite. However, only the sulphatisation and alkali method are commonly used in commercial production. The sulfuric acid method was once applied on an industrial scale in the United States. Currently, this method is being applied to low grade monazite and xenotime at the Lynas plant in Gebeng, Malaysia. The sulfuric method has been superseded by alkali method in recent years, which has been applied in industrial production in many countries such as India (Indian Rare Earths Ltd – IRE)[1], France (La Rochelle)[1, 2], Malaysia (Asian Rare Earth Sdn Bhd - ARE)[3], United States (Freeport, Texas)[4], Brazil (Santo Amaro - USAM)[5, 6]...

In Vietnam, the alkali method has been researched and deployed on pilot scale in the Indian pilot line (60 tons/year), which was transferred by the Indian government to Institute for Technology of Radioactive and rare elements (ITRRE) in 1991. ITRRE has operated, researched, supplemented and completed the technological process within the framework of the state-level project (KC-09-12). However, there were many difficult problems and challenges in the 1990s due to the limitations of equipment and technology, such as: 1) the requirement of fine grinding of monazite concentrate to 325 mesh (<45 μm); and 2) the decomposition time of monazite extended from 8 to 10 hours for particle size of ~200 mesh so that the decomposition efficiency reached 93%.

New decomposition methods have been proposed to overcome the limitations of the

traditional alkali method, the most typical of which is the decomposition baking method with new agent KOH. Kumari et al. (2019)[7] have decomposed Korean monazite concentrate by KOH pellet and obtained some results showing the advantages of the new method. Following those studies, the monazite research group of Institute for Technology of Radioactive and Rare Elements (ITRRE) conducted the investigation KOH decomposition baking method applied to Vietnamese monazite. The purpose of the research was to implement deep processing Vietnamese monazite in industry, hence the non-grinding concentrate and industrial alkaline KOH flake were used.

II. CONTENT

A. Object and methods

The investigation's object is Vietnamese monazite concentrate, which is exploited and supplied by Hung Thinh Titanium Slag Factory in Binh Thuan. Before conducting decomposition baking, the monazite concentrate was determined

the crystalline phase composition by X-ray diffraction (XRD) method, the elemental composition by chemical combined with Inductively coupled plasma - optical emission spectrometry (ICP-OES) method.

An amount of 10g of monazite concentrate (non-grinding) was mixed with industrial flake KOH in a 50mL nickel crucible with KOH:monazite mass ratio of 0.8, 1.0, 1.2, and 1.5, corresponding to the theoretical residue of 114, 143, 171, and 214%. The mixture was then baked in a Nabertherm L 9/12/P320 given at 200, 250, 300, and 400°C for 0.5, 1, 2, and 3 hours. The residue after baking was slurred by adding water for 3-4h. and washed by ambient temperature water to remove all phosphate and residual alkaline, then completely dissolved in concentrated hydrochloric acid. The remaining insoluble residue was analyzed mass, composition (by ICP-OES method), and crystal phase (by XRD method). The experimental scheme is given in Figure 1 and the performance calculations are in formula (1) and (2).

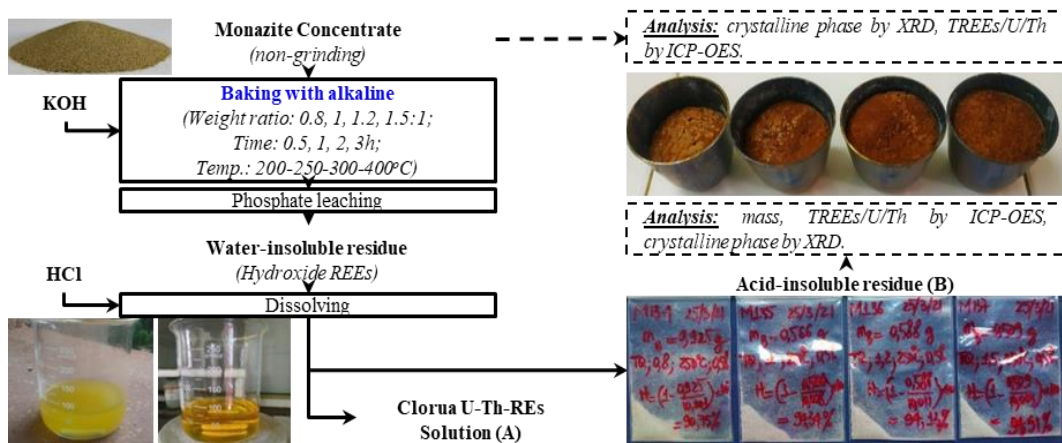


Fig. 1. Experiment diagram of alkaline decomposition baking for Vietnamese monazite concentrate

$$\text{Decomposition efficiency of monazite conc.} = \left(1 - \frac{\text{Weight of residue (B)}}{\text{Weight of monazite concentrate}}\right) \times 100\% \quad (1)$$

Conversion efficiency of TREES-U-Th

$$= \left(1 - \frac{\text{TREES-U-Th content (\%) in residue (B)} \times \text{Weight of residue (B)}}{\text{TREES-U-Th content (\%) in monazite concentrate} \times \text{Weight of monazite concentrate}}\right) \times 100\% \quad (2)$$

B. Results

1. The chemical composition of monazite concentrate

The Vietnamese monazite concentrate was analyzed the phase composition by XRD

method (Figure 2). The preliminary XRD analyzes showed that the phase composition of the concentrate coincided with the monazite-Ce sample (RRUFF ID R040106)[8].

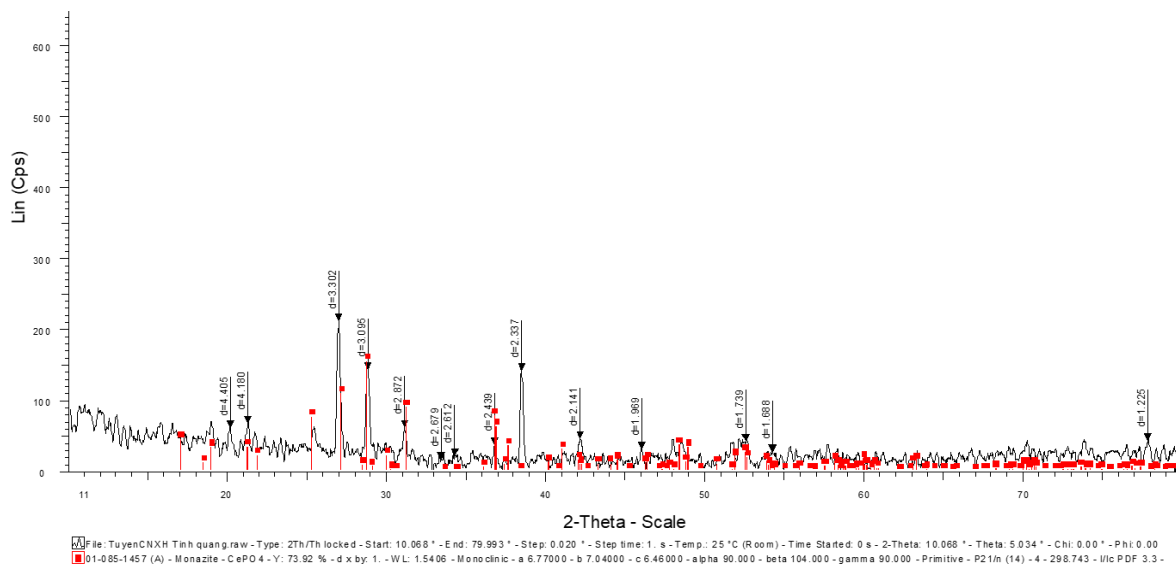


Fig. 2. XRD pattern of Vietnamese monazite concentrate

The monazite sample was analyzed total rare earth elements (TREEs), uranium (U) and thorium (Th) by the chemical combined with ICP-OES methods. The feed concentrate was completely digested in a platinum crucible at 700°C for 3 hours by mixing with pure alkaline (NaOH) with NaOH:concentrate mass ratio of 50 to 100:1. The crucible was shaken to increase agitation approximately every 30 min during the reaction, then obtained mixture was completely converted into solution by concentrated HCl acid and diluted to conduct ICP-OES measurement.

Table I shows the elemental composition of monazite concentrate. The total rare earth (TREEs) content reached 44.81%, which was lower compared to the theoretical concentration (~58%) with the general formula (LREs, Th)PO₄. The uranium (U) content was insignificantly small because U is an accompanying minor component. The thorium (Th) content was about 4.49%, which is typical for Vietnamese monazite. Other impurity elements such as iron (Fe), titanium (Ti), zircon (Zr) had negligible contents.

Table I. Analysis results of total rare earth elements (TREEs), uranium (U), thorium (Th), and some impurities (Fe, Ti, Zr) by combined chemical and ICP-OES methods

Elements	LREEs					Y	TREEs	U	Th	Impurities		
	La	Ce	Pr	Nd	Sm					Fe	Ti	Zr
Content (wt.%)	9.66	21.63	2.19	7.4	1.28	0.98	44.81	0.34	4.49	0.09	0.02	-

2. Effect of the KOH:monazit mass ratio, baking time, and baking temperature on the decomposition efficiency of monazite concentrate, scale of 10 g/batch

The 10g/batch scale banking experiments were performed sequentially as shown in Figure 1. The final insoluble residue (B) after each experiment was mass analyzed, then the decomposition efficiency of monazite concentrate was calculated by formula 1.

Figure 3a shows the effect of KOH:monazite mass ratio on the decomposition efficiency of monazite concentrate. The decomposition efficiency was in the range from 93 to 95% when the KOH:monazite mass ratio was 1:1. This efficiency was significantly

higher than the efficiency at the ratio of 0.8 (86-90%); and was not significantly lower than the efficiencies at ratio of 1.2 and 1.5 (94-96%). Therefore, the optimal KOH:monazit mass ratio was 1:1.

Figure 3b shows the effect of baking temperature on the decomposition efficiency of monazite concentrate. The decomposition efficiency was in the range from 94 to 95% when the baking temperature was 250°C. The efficiency was significantly higher than the efficiencies at the temperature of 200°C (86-90%); and even slightly higher than the efficiencies at temperatures of 300 and 400°C (94-96%). Therefore, the optimal KOH baking temperature was 250°C.

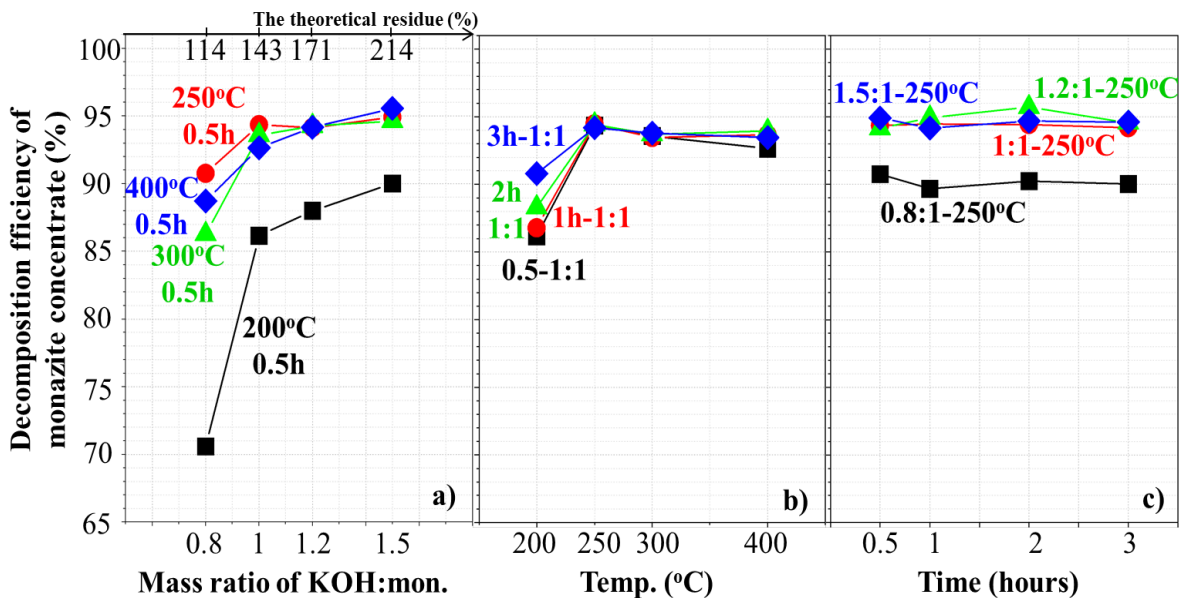


Fig. 3. Effect of KOH baking conditions on the decomposition efficiency of monazite concentration a) KOH:monazite mass ratio; b) baking temperature; and c) baking time

Figure 3c shows the effect of baking time on the decomposition efficiencies of monazite concentrate. It is easy to see that the decomposition efficiencies of monazite concentrate after 4 time periods are similar. This proves that the optimal KOH decomposition calcination time is only 0.5 hours.

From the analyzed results, the optimal KOH baking conditions for monazite concentrate are 1:1 of mass ratio, 250°C of temperature, and 0.5 hours of time. The decomposition efficiency of monazite concentrate at the scale of 10 g/batch at the optimal baking conditions reached 94%.

3. Effect of optimal decomposition baking conditions on the conversion efficiency of total rare earth, uranium and thorium (TREEs-U-Th), scale of 100 g/batch

The 100g/batch scale experiments were conducted at the optimal decomposition baking conditions, which were obtained from the 10g/batch experiment scale. The experiments were carried out in a 304-stainless-steel-crucible with a capacity of 500mL and a bottom diameter of 95mm. The

experimental sequences were performed in the same way as the 10g/batch scale experiment. As a result, the final insoluble residue (B) was obtained with a mass between 5 and 7 g. Visual characteristic of residue B was white, which is different from the yellow color of monazite concentrate. The residue was analyzed chemical method combined with ICP-OES. Table 2 shows the ICP-OES analysis results of residue B and the original monazite concentrate sample.

Table III. Analytical results of total rare earth elements (TREEs), U, Th in insoluble B residue and yields (scale of 100g/batch – the decomposition baking conditions: monazite non-grinding; mass ratio of KOH :monazite concentrate is 1:1; temperature 250°C; and time of 0.5 hours)

Mass (g)	Content (wt.%)								
	LREEs					Y	TREEs	U	Th
	<i>La</i>	<i>Ce</i>	<i>Pr</i>	<i>Nd</i>	<i>Sm</i>				
4.218	1.21	2.24	0.22	0.73	0.12	0.12	4.80	0.02	1.10

The decomposition efficiency of monazite concentrate was calculated from the results of mass analysis Table 2 according to formula 1 in section 2.1. The results show that the decomposition efficiency by KOH was high, reaching 96%. Compared with the results in the scale of 10 g/batch, the result shows no significant difference.

Similarly, the conversion efficiencies of TREEs-U-Th were calculated according to

formula 2 in section 2.1. The conversion efficiencies were high in range of 98 to 100%, which was higher than the decomposition efficiency about 4 to 5%. This difference can be explained as follows: the monazite concentrate contains other minerals that were not completely decomposed in the decomposition baking condition and left after dissolving the hydroxide residue with HCl (residue B).

Table IV. The decomposition efficiency of monazite concentrate and conversion efficiencies of TREEs-U-Th

Decomposition efficiency (%)	Conversion efficiency (%)								
	LREEs					Y	TREEs	U	Th
	<i>La</i>	<i>Ce</i>	<i>Pr</i>	<i>Nd</i>	<i>Sm</i>				
95.8	99.5	99.6	99.6	99.6	99.6	99.5	99.6	99.7	99.0

4. The phase composition of residue B

The residue B was further analyzed XRD to determine the mineral form. Figure 4 shows the XRD pattern of residue B, the sharp and intense spectral peaks are completely separated from the

background. Comparison with the XRD spectrum of the zircon ($ZrSiO_4$) standard sample (RRUFF ID R050034)[9] shows that the characteristic peaks coincide. This proves that the residue B is mainly composed of zircon ($ZrSiO_4$).

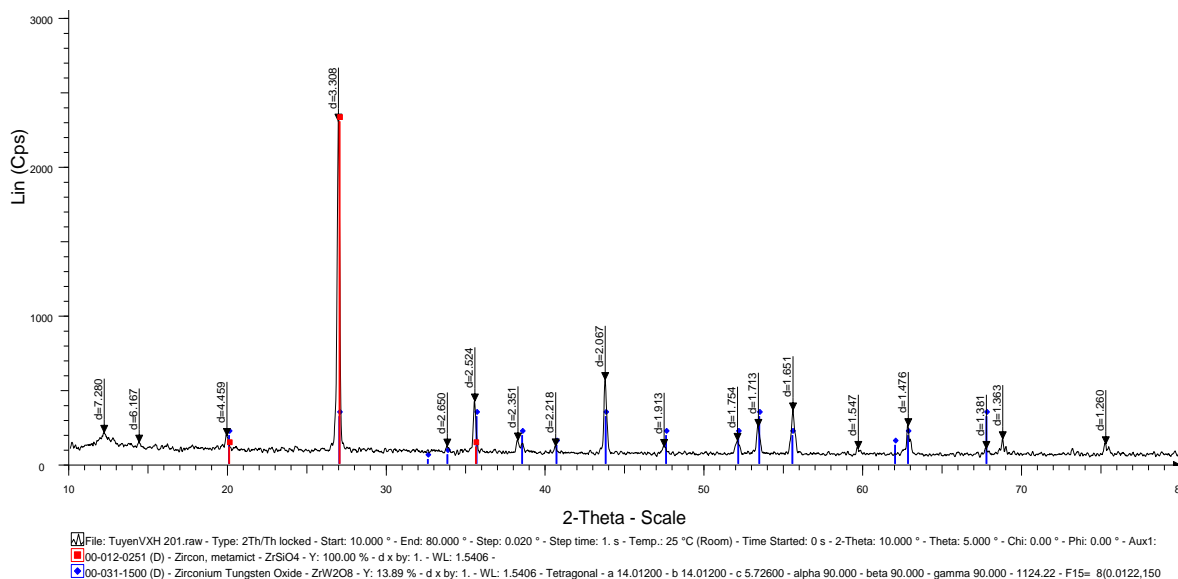


Fig. 4. X-ray diffraction (XRD) pattern of insoluble residue B compared with zircon's XRD pattern from Oaxaca - Mexico[9]

In fact, the zircon mineral is the main component of coastal placer along with ilmenite, which is separated and recovered before monazite. The mineral is relatively stable when baking by alkaline under the conditions that are conducted at temperatures in range of 200 to 400°C. According to the published literatures, the temperature for the decomposition reaction of zircon to take placesignificantly is around 650°C.

C. Discussion

The baking efficiency of decomposing monazite concentrates by KOH varied widely from 70 to a maximum threshold of 95%. Optimal conditions were determined from the results in 10g/batch experimental studies, and the experiment was scaled up to 100g/batch. The insoluble residue B obtained after the experiments were analyzed mass, elemental and

phase composition. The concentrate decomposition and TREEs-U-Th conversion efficiency were calculated from the results of mass and chemical composition analysis. The TREEs-U-Th conversion efficiencies are all high in the range of 99 to 100%, which indicates that the monazite concentrate decomposed almost completely.

The monazite decomposition, TREEs-U-Th conversion efficiencies at optimal baking conditions were compared with the efficiency in some other results, which were shown in Table 4 such as the Indian alkaline method (Vietnamese monazite), high-pressure alkaline method (Vietnamese xenotim) and KOH baking method (Korea monazite). The results show that the method of baking monazite with KOH performed in the current study has many advantages.

Table V. Comparison of current research results on optimal conditions to other technologies

Technology Parameters	NaOH leaching (1991) – Vietnamses monaz. conc.[10]	NaOH (12.5M) leaching (2001-2002) – Vietnamses monaz. conc.[11]	KOH (pellet) baking (2019) – Korean monaz. conc.[7]	NaOH (flake) baking (2021) – Vietnamses monaz. conc.	KOH (flake) baking (2021) – Vietnamses monaz. conc.
Particle size (mesh)	200 (75 μ m)		100-150 (100-150 μ m)	140 – 70 (100-200 μ m) non-grinding	
Reagents	NaOH solution		KOH pellet	NaOH flake	KOH flake
Alkaline:concentrates mass ratio (w:w)	0.9:1 (180%)	2:1 (400%)	1:1 (143%)	1.2:1 (240%)	1:1 (143%)
Temperature (°C)	135-140	200 (10.5atm) 240 (20atm)	250	400	250
Time (h.)	8-10	4	0.5	1	0.5
Efficiency (%)	93 (8h)	90 (10.5atm) 94.7 (20atm)	Phosphate: ~100	Monazite: 96 TREES/U/Th: 99-100	

The first advantage of alkaline (KOH) baking method for monazite concentrate is the direct utilization of non-grinding monazite concentrate, which brings many advantages such as saving investment costs in crushing equipment and equipment maintenance costs; saving grinding time, thereby reducing labor; saving grinding energy costs (because of high hardness monazite concentrate, ultra-fine grinding of concentrate to size 325mesh consumes a lot of power); and reducing the risk of radioactive fallout to a minimum by omitting the ultrafine grinding of the ore...

Other advantages are that the decomposition temperature of 250°C is not too high in the industry compared to the alkaline hydrometallurgical temperature of NaOH 135-140°C and the high-pressure alkaline hydrometallurgy temperature of 200°C. The baking time to decompose by KOH is also very

short, only 0.5 hours, which is 8 to 20 times lower than the hydrometallurgical methods. The shortening of time saves energy and is suitable for the deployment of many batches per day in the actual production.

III. CONCLUSION

The optimal baking conditions of Vietnamese monazite concentrate(non-grinding) by KOH flakes were determined as follows: (1) 1:1 of KOH:monazite mass ratio; (2) 0.5 hours of baking time; (3) 250°C of baking temperature. The decomposition efficiency of monazite concentrate was 92 to 95% and the conversion efficiencies of TREES-U-Th were 99 to 100% at optimal conditions at the experimental scale of 100g/batch. The initial results show the great technological potential of the KOH alkaline baking method, which can replace the old Indian method in the future if it is researched scale-up studies.

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