

Characteristics of Treated Monazite in Different Particle Sizes to Upgrade the Rare Earth Elements Content by Using Mechanochemical and Roasting Processes

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Abstract. Rare earth metals (REE) constitute one of the most crucial groups of elements globally. In Indonesia, deposits of REE have been recognized within monazite minerals extracted from tin mining operations in Bangka. Nevertheless, Indonesia has not used these deposits and has instead heavily relied on imports from other countries. This study aims to recover rare earth metals, specifically Cerium (Ce), Lanthanum (La), Ytterbium (Yb), and Yttrium (Y), from monazite sand, a by-product of tin mining. The method employed in this research is Mechanochemical Decomposition, involving the reaction of monazite samples with a 33 wt% solid Sodium Hydroxide (NaOH) to convert REE-Phosphate compound into REE-Hydroxide. The process begins with sample preparation, involving mechanochemical decomposition using a ball mill, followed by roasting at 400°C, leaching with distilled water, and subsequent steps of filtration and drying at 120°C. Various initial particle sizes, denoted as +65, -65 +100, -100 +140, -140 +170, and -170 mesh, were used to assess their effect on the recovery and grade of REE. Various initial particle sizes, denoted as +65, -65 +100, -100 +140, -140 +170, and -170 mesh, were used to assess their effect on the recovery and grade of REE. The series of procedures revealed notable improvements in the REE content in monazite. The highest recovery of Ce, La, Yb, and Y elements reached 46.43%, 70.08%, 22.69%, and 23.31%, while the highest grade of those elements obtained the values of 4.116%, 1.543%, 0.263%, and 1.681%, respectively. In alignment with prior research, the recovery of Light Rare Earth Elements (LREEs) surpasses that of Heavy Rare Earth Elements (HREEs). However, a unique observation emerges: a diminishing trend in both recovery and grade as particle sizes become finer. This unexpected phenomenon warrants further investigation to elucidate the mechanisms governing rare earth metal recovery from monazite sand under varying particle sizes.

Keywords: By-product; Monazite; Particle size; REE-Oxide; Roasting

1. Introduction

Rare earth metals (REE) are a mineral group consisting of 17 elements, namely 15 elements of the lanthanide group (La – Lu), Scandium (Sc), and Yttrium (Y) (Van-Gosen *et al.*, 2014). The abundance of REE in the earth's crust is significant but not concentrated at one point (Lide, 2005). This causes the extraction of REEs as the main product does not have high economic value and is currently only extracted as a by-product (Gupta and Krishnamurthy, 2005). In the world, REE production is dominated by China by 90%, with

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minerals in the form of monazite and bastnasite (Bünzli and Pecharsky, 2016). Meanwhile, Indonesia currently imports 100% of its REE needs from countries such as China, Japan, Malaysia, and others (Ministry of Energy and Mineral Resources, 2020). Research from the Ministry of Energy and Mineral Resources stated that Indonesia has 180,000 tons of monazite reserves and 20,000 tons of xenotime in the Bangka and Belitung Islands. These reserves must be utilized to meet domestic needs, where the REE industrial sector is projected to increase from USD 2,831 million in 2021 to USD 5,520.2 million in 2028 (Fortune Business Insight, 2021). In Indonesia, research regarding REE is carried out not only from Monazite and Xenotime but also from by-product raw materials such as Zircon tailings, as reported by Prameswara *et al.* (2023) and Trisnawati *et al.* (2020), it can also be found in coal-related by-products such as fly ash from coal combustion reported by Prihutami *et al.*, 2021.

Trisnawati *et al.* (2020) reported that Y, Gd, Er, Dy, and Yb as HREEs₂-(SO₄)₃ products can be recovered through sulfuric acid leaching, while the result from Prameswara *et al.* (2023) showed that Dy and Yb leaching from solid REE-hydroxide using HCl solution afforded a total of 61.71% Dy and 74.55% Yb recovery. The processing of REE from monazite can be achieved through chemical treatment, employing acid and base methods. Two common approaches involve NaOH digestion or leaching with H₂SO₄ to extract REE from monazite (Habashi, 2013). In addition to hydrometallurgical processing, pyrometallurgical processes use Ca or Mg-reducing agents through Metallothermic methods. In this study, a mechanochemical decomposition process was used, namely a reaction process that utilizes mechanical forces. The mechanochemical process has advantages, such as lower energy consumption, freedom of liquids, and absence of by-products (Mateti *et al.*, 2021). In addition to mechanochemical, a roasting process is carried out to produce REE-Oxide and complete the reaction of NaOH with monazite.

In a few studies, the researcher has used mechanochemical processes, especially inorganic material. For instance, Bonnaillie *et al.* used the mechanochemical method for synthesizing SnO₂ nanostructures (Legendre, Poissonnet, and Bonnaillie, 2007). The other, Tsuzuki and McCormick, use this process for nanoparticle synthesis and mechanical alloying (Tsuzuki and McCormick, 2004). Nowadays, the process is barely used in mineral processing, such as monazite sand (Kim *et al.*, 2009). Kim *et al.* add the mechanochemical using NaOH to assist the leaching process (Kim *et al.*, 2009). The result shows the formation of REE-hydroxide from REE-phosphate. On the other hand, Kumari *et al.* used NaOH during roasting at 400°C, continued with leaching, and showed promising REE recovery (Kumari *et al.*, 2015).

This study aims to increase Ce, La, Yb, and Y grades on monazite from cassiterite ore by-products using various particle sizes ranging from coarser than 65 mesh to finer than 170 mesh. The process includes mechanochemical for sample preparation and REE hydroxide formation, continued with roasting for REE oxide formation. The highlighted result of this study is the determination of the appropriate particle size of monazite for the mechanochemical-roasting process, which aims to enhance the content of Ce, La, Yb, and Y.

2. Methods

2.1. Sample Preparation

Monazite sand was preliminarily dried at 80°C and subsequently underwent size reduction through ball milling, with a rotational speed ranging from 67.8 to 71.1 rpm over a 30-minute duration. The milling process yielded five distinct particle size fractions, specifically +65 mesh, -65 to +100 mesh, -100 to +140 mesh, -140 to +170 mesh, and -170 mesh.

2.2. Mechanochemical with NaOH 33wt%

Each particle size fraction was subjected to a mechanochemical treatment with the incorporation of 33 wt% sodium hydroxide (NaOH) from Pro Analys Merck 106498. The purpose of adding NaOH was to react with rare earth element phosphate (REE-PO₄) and produce rare earth element hydroxides (REE-OH). The mechanochemical process was conducted within a ball mill from NOAH NQM-4, employing a rotational speed of 650 rpm for a duration of 120 minutes.

2.3. Roasting

Before the roasting step, the mechanochemically treated samples were subjected to compaction using a Krisbow Hydraulic Press, thereby increasing the contact surface area. Subsequently, the roasting procedure was conducted in a Payun Tech Muffle Furnace within alumina crucibles, sustained at a temperature of 400°C for a duration of 120 minutes. This process served the dual purpose of finalizing the NaOH and REE-PO₄ reaction and facilitating the oxidation of rare earth elements inherent in the sample.

2.4. Distilled water washing, filtration, and drying

The roasted product was subjected to leaching with distilled water at a controlled temperature of 70°C and a rotational speed of 680 rpm, maintained for a duration of 30 minutes, which was discussed in the next section as a washing process. The process was conducted by a Hot Plate Magnetic Stirrer from Thermo Scientific Cimarec SP88857105. The primary objective of this step was to facilitate the dissolution of the formed Na₃PO₄ compound. Following completion of the leaching process, the mixture was subjected to filtration, yielding a precipitate. This precipitate was subsequently isolated and subjected to drying at 120°C for 120 minutes using Memmert UN 55 Oven.

2.5. Characterization

To identify the REE content in the initial sample, the ICP-OES test was conducted at Laboratorium Teknologi Bahan Galian Nuklir National Research and Innovation Agency (BRIN). X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) analyses were conducted on dried samples as part of a comprehensive characterization step. The objective of the XRD analysis, undertaken at the Center for Materials Processing and Failure Analysis (CMPFA) at Universitas Indonesia, and the XRF is conducted at the Laboratory of the National Research and Innovation Agency (BRIN), focused on quantifying the concentration increments of key elements, specifically Cerium (Ce), Lanthanum (La), Ytterbium (Yb), and Yttrium (Y). These analyses collectively provided essential insights into the composition and elemental content of the investigated specimens, contributing to a comprehensive understanding of their properties and potential applications.

3. Results and Discussion

3.1. Monazite Raw Sand Characteristics

Following the method outlined by Zhang and Noble, the initial monazite is characterized using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). (Zhang and Noble, 2020). In this study, the REEs content detected by the characterization process involved ICP-OES present in the monazite sample is shown in Table 1. Cerium exhibited the highest concentration among the other REEs, followed by several other Light Rare Earth Elements (LREEs), as summarized in Table 1.

Before the mechanochemical and roasting processes, sample preparation was carried out on the monazite. Firstly, the monazite was subjected to a drying process to eliminate any residual moisture present (Jung, Lee, and Yoon, 2018). Subsequently, size reduction was performed to obtain monazite particles of specific sizes: +65mesh, -65mesh +100mesh,

-100mesh +140mesh, -140mesh +170mesh, and -170mesh. The obtained five different particle sizes underwent further characterization through X-ray Fluorescence (XRF) analysis. This analysis served to determine the content of cerium (Ce), lanthanum (La), yttrium (Y), and ytterbium (Yb), as presented in Table 2. The XRF results also provide information about the dominant elements present in the sample, including silicon (Si), iron (Fe), and tin (Sn).

Table 1 ICP-OES results of initial monazite samples

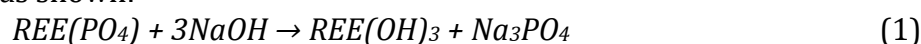
Elements	Ce	La	Nd	Pr	Sm	Y	Gd	Dy	Sc	Tb	Eu	Yb
Concentration (ppm)	8927	4189	2860	1750	737.3	436.4	161.8	158.3	23.7	6.8	2.8	0.14

Table 2 XRF results of the initial monazite sample

Particle Size (mesh)			-65mesh	-100mesh	-140mesh	-
	+65mesh	+100mesh	+140mesh	+170mesh	170mesh	
Concentration (wt%)	Ce	0.759	1.165	0.801	0.878	0.898
	La	0.174	0.279	0.203	0.218	0.206
	Y	0.958	0.595	0.642	0.628	0.767
	Yb	0.154	0.089	0.082	0.089	0.102

3.2. Converting Rare Earth Phosphate to Rare Earth Hydroxide

In order to decompose phosphates in REE, monazite is milled with the addition of NaOH. The milling process took place in a planetary ball mill for 120 minutes at 680 rpm, serving two primary purposes: mixing and milling. Monazite is mixed well with NaOH during milling, while the mechanical force helps break bonds between REE and phosphates. NaOH will react with phosphate, producing REE hydroxides and Na₃PO₄ (Kim *et al.*, 2009). The mixture changes in color from light grey and white to dark grey. Besides that, the photo shows some agglomeration in the mixture. This might be caused by NaOH's characteristic of being hygroscopic (Ahmadi and Seyedin, 2019). The reaction occurs during mechanochemical is as shown:



Besides that, NaOH also reacts with CO₂ in the atmosphere, creating Na₂CO₃ as a product (Monash Scientific Glass Blowing Services, n.d.). The reaction occurs as shown:



3.3. Roasting in atmospheric condition

This process aims to change hydroxide from mechanochemical to oxide compound. The method includes heating samples at 400°C for 2 hours in the atmospheric condition. The reaction that occurs during roasting is as shown:



The result shows the change in morphology and color. The pellets show expansion and shift in color from dark grey to yellow-greenish. Expansion on +65mesh and -65mesh +100mesh seen are much more significant than the rest. Lower expansion on -100mesh +140mesh, -140mesh +170mesh, and -170mesh is caused of denser pellets. Expansion might occur because of CO₂ formation during the reaction between phosphate and Na₂CO₃, as shown in equation 1 (Kumari *et al.*, 2015). In addition, the expansion might appear because of the voids left from compaction that expand during the heating/roasting process.

The reaction can be validated with XRD, where REE was found in the oxide form. XRD also shows Na in Na₃PO₄ and Na₂CO₃ form, which indicates equations (1) and (2) have

occurred. SnO_2 , SiO_2 , Fe_3O_4 , and FeTiO_3 are monazite impurities as a cassiterite by-product, as shown in Figure 1 (Harjanto, Virhdian, and Afrilinda, 2013).

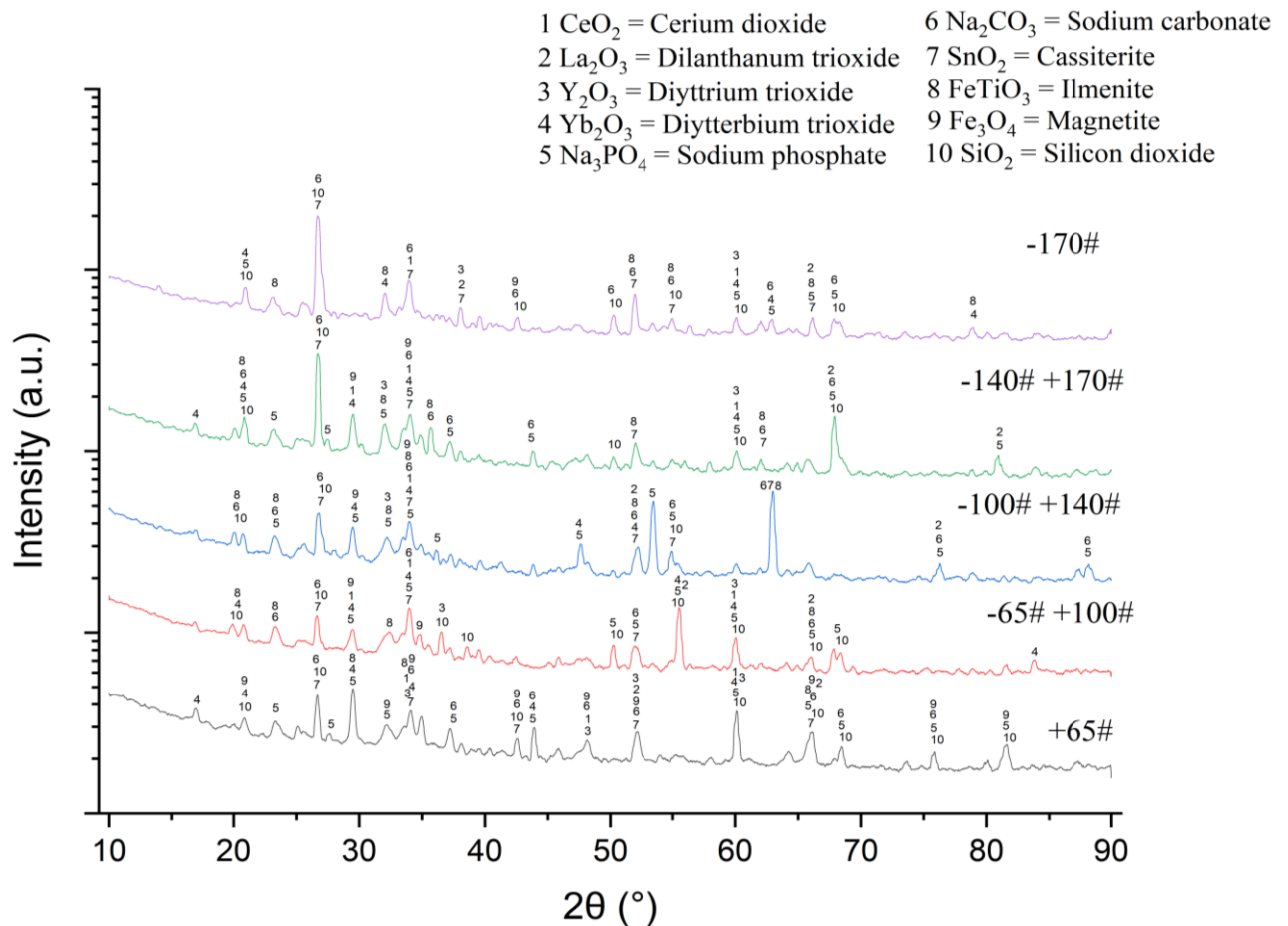


Figure 1 XRD results after the roasting process.

3.4. Leaching with distilled water to dissolve Na_3PO_4

Na (Na_2CO_3 and Na_3PO_4) dissolve in water. Therefore, the by-product will dissolve by agitating the sample in distilled water, leaving only REE residue (Kim *et al.*, 2009; PubChem, n.d.). Leaching is done at 70°C for 30 minutes at 680 rpm. The results show changes in color from yellow-greenish to brown-reddish, while the morphology does not.

XRD shows that Na is still present as Na_2CO_3 and Na_3PO_4 , indicating insufficient washing time. On the other hand, the REEs and impurities compound's form doesn't change. The analysis results of the XRD pattern are shown in Figure 2. Upon completion of the washing and drying processes, an analysis of the residue revealed an increase in the concentration levels of elements Ce , La , Y , and Yb . The X-ray Fluorescence (XRF) characterization results presented in Table 3. demonstrate the observed changes in element concentrations.

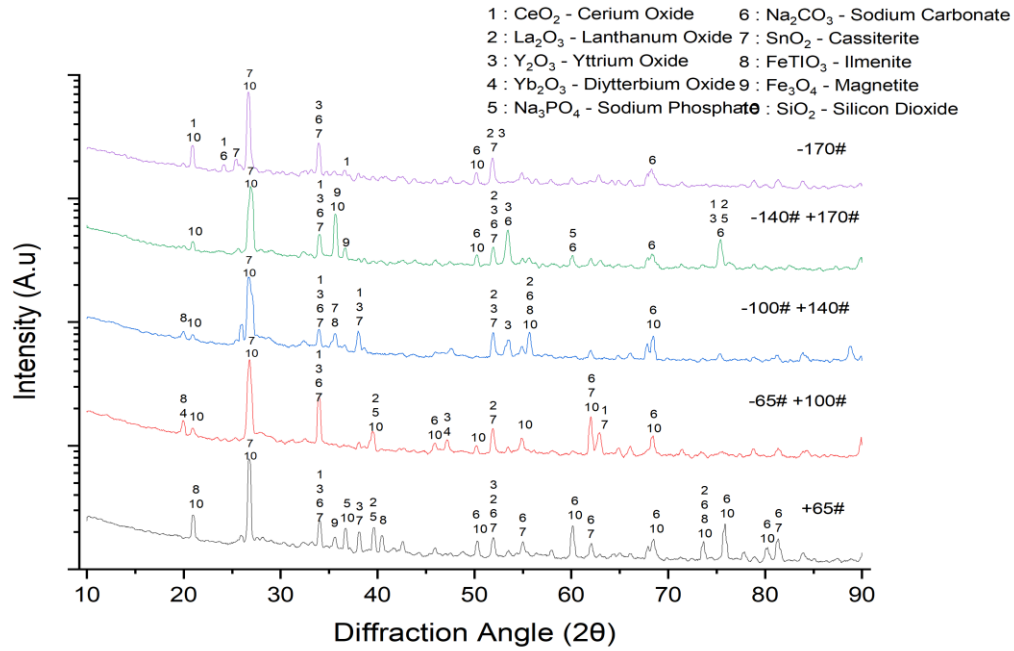


Figure 2 XRD results after distilled water washing and drying

Table 3 XRF result of the product after distilled water washing and drying

Particel Size (mesh)		+65mesh	-65mesh +100mesh	-100mesh +140mesh	-140mesh +170mesh	- 170mesh
Concentration	Ce	2.653	4.116	3.829	1.861	1.376
(wt%)	La	0.915	1.543	1.452	0.548	0.323
	Y	1.681	1.006	1.171	0.972	0.960
	Yb	0.263	0.159	0.148	0.117	0.108

3.5 Product Morphology after roasting and after the leaching process

SEM results with 1000 x magnification of the sample after the roasting process can be seen in Figure 3. Meanwhile, the SEM results with 1000 x magnification of the sample after the washing and drying process can be seen in Figure 4. According to EDS result, in the samples after the washing process with sizes -100mesh +140mesh and -170mesh, the Ce content was 33.17% and 0.92%, respectively. Meanwhile, other samples did not show any REE content.

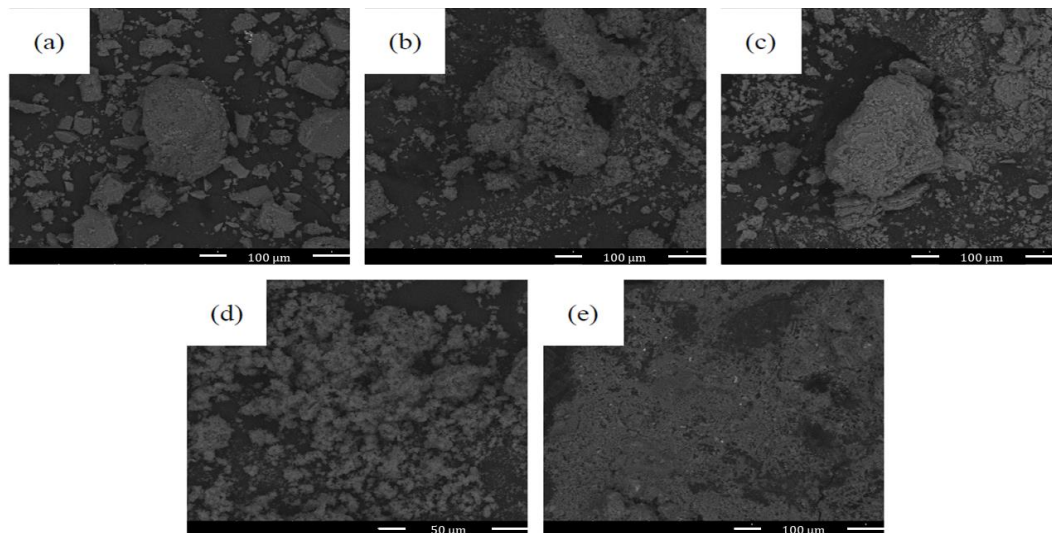


Figure 3 SEM results after roasting for particle size (a) +65mesh (b) -65mesh +100mesh (c) -100mesh +140mesh (d) -140mesh +170mesh (e) -170mesh

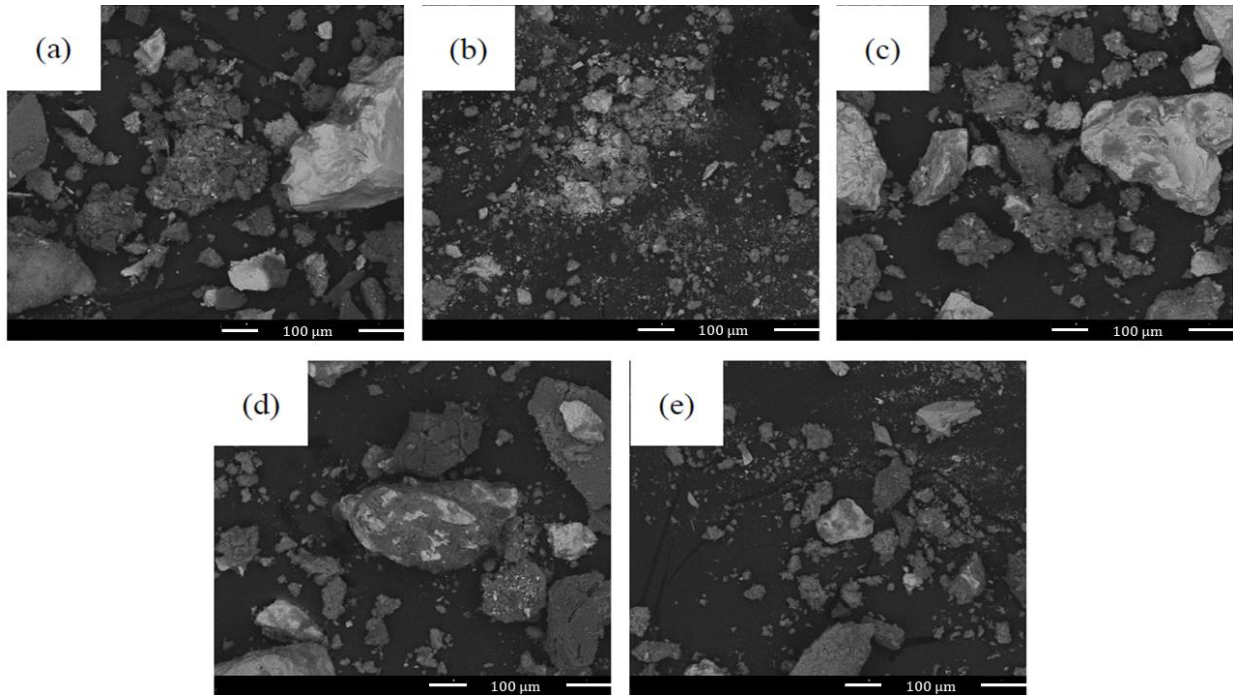


Figure 4 SEM results after washing for particle size (a) +65mesh (b) -65mesh +100mesh (c) -100mesh +140mesh (d) -140mesh +170mesh (e) -170mesh

Table 4 EDS result of the product after distilled water washing and drying

Particle Size (mesh)	+65mesh	-65mesh +100mesh	-100mesh +140mesh	-140mesh +170mesh	- 170mesh	
C	2.48	2.85	2.01	1.26	1.84	
O	32.87	33.21	29.31	22.68	33.45	
Na	2.04	13.99	9.88	2.30	6.24	
Mg	0.19	0.11	-	0.52	0.78	
Al	0.41	2.15	1.03	0.57	1.59	
Si	2.9	16.3	9.07	1.54	5.26	
Concentration (wt%)	S	0.96	2.15	1.41	0.42	1.06
	Sn	51.12	6.40	3.31	67.09	39.80
	Ca	0.81	0.25	0.24	1.29	0.07
	Ti	0.73	2.47	1.77	0.29	0.38
	Fe	4.77	19.90	8.21	1.58	7.53
	Ni	0.71	0.21	0.60	0.46	0.48
	Ba	-	-	-	-	0.61
	Ce	-	-	33.17	-	0.92

%recovery calculation was done on the final product using REE contents based on equation (4).

$$\%Recovery = (wt\% \times Product\ Mass) / (wt\% \times Feed\ Mass) \times 100\% \quad (4)$$

The result of the %recovery calculation from Ce, La, Y, and Yb is present on a graph shown in Figure 5. Based on that picture, the coarser the initial particle size, the higher %recovery will be earned. This phenomenon can be attributed to the fact that samples with finer particle sizes tend to experience greater losses during the processing stages, resulting in higher weight loss percentages.

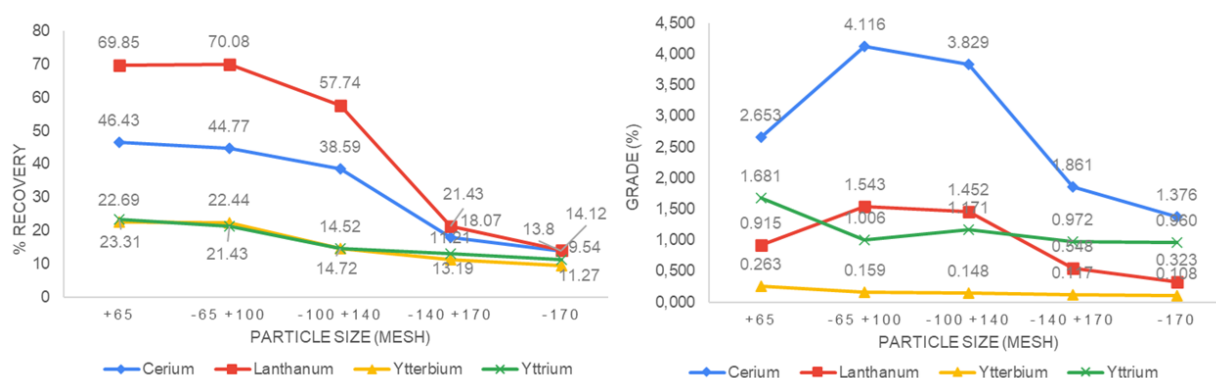


Figure 5 Effect of initial particle size on (a) %recovery and (b) %grade of Ce, La, Y, and Yb

4. Conclusions

Monazite contains REE, mainly LREE. Sn, Fe, and Ti present as impurities. NaOH is an effective reagent used for mechanochemical decomposition to remove phosphate from monazite by reacting and producing Na_3PO_4 . Ce, La, Yb, and Y had their content increased after the procedure. The highest %grade of Ce and La achieved at particle size -65mesh +100mesh respectively by 4.116% and 1.543% each. Yb and Y have the highest %grade at particle size +65mesh, respectively, by 0.263% and 1.681% each. The highest %recovery of Ce, La, Yb, and Y was achieved at particle size +65mesh by 46.43%, 70.08%, 22.69%, and 23.31% respectively, which have the final form of CeO_2 , La_2O_3 , Yb_2O_3 , and Y_2O_3 .

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