Baking process of mineral carrier of rare earth metals with sodium hydroxide using muffle furnace

M Setyadji¹ and H F Nurly²

¹Center for Accelerator Science and Technology-BATAN Babarsari Street Pos Office Box 6101 ykbb, Yogyakarta 55281, Indonesia
²Department Metallurgy Engineering, Sultan Ageng Tirtayasa University Jendral Soedirman Street Km03, Cilegon 42435, Indonesia

E-mail: mstyadji@batan.go.id

Abstract. Rare Earth Elements (REE) is one of the natural resources that are very strategic and high economic value. REE applications in industry are continues to grow such as LCD (liquid crystal display), LED (light emitting diode), magnet and hybrid batteries (NiMH batteries; Misch metal; Ce, La, Nd). This resulted in REE demand continues to increase up to 10%. Increased demand is not matched by the number of Rare Earth production in the world. This happens because the Chinese as the main actor in the producer REE world production (95%) restricting the export of Rare Earth up to 35% so that the world price of LTJ bounced up. Research & development processing, and purification REE continue to obtain high purity Rare Earth Metals. Baking process the mineral carrier of REE (raw material minerals) with solid NaOH using a muffle furnace has been carried out. The research aims to determine the effect of temperature and grain size of the monazite sand on the decomposition reaction monazite sand and reaction kinetics. The raw materials used are monazite sands containing rare earth oxides as much as 55.1% and 11.01% phosphate. At monazite sand baking using solid NaOH will occur monazite sand decomposition process and the release of the existing phosphate. The results showed that the optimal conditions baking process at a temperature of 400°C and 200 mesh particle size obtained 91.40% phosphate inseparable.

1. Introduction
Rare earth metals are a group of 15 lanthanide metals including yttrium and scandium. Rare earth metals have unique characteristic in particular spectroscopic and magnetic properties [1]. Rare earth metals have very important application in industry such as permanent magnetic materials, electronics, super-conductors, medical and nuclear technology. Rare earth metals have some unique properties of saturated 4f electronic structure that allow them to be used in luminescence-, magnetic- and electronic devices [1,2,3]. Geologically speaking, Rare Earth Minerals are not found on the earth as a free element, but as alloys in the form of complex compounds. Rare Earth Minerals are grouped into mineral carbonates, phosphates, oxides, silicates and fluorides [4-6]. One of the Rare Earth Minerals that has been extracted or mined in Indonesia in the form of phosphates are the monazite sand ((Ce, La, Nd, Pr, Sm) PO₄) and the xenotim sand ((Y, Dy, Gd, Sm) PO₄) [7]. Indonesia has an abundance of raw materials of local natural resources that have the potential to be processed into useful products for human need which has high economic value.
According to the results of the review in geology in 2013, the potential reserve of rare earth metal based monazite sand mineral commodity is relatively abundant on the islands of Bangka and Belitung, and is quantitatively estimated to be 1,564,707,280 tonnes (inferred resources) and 3,100,000 tonnes (probable reserves). With this vast reserve and also in reference to the conditions, rules and regulations specified in the Department of Energy and Mineral Resources Ministerial decree (ESDM Minister No. 7 of 2012) regarding the required specification that the final products of the metallurgical process must achieve high purity limits; and also in accordance with the specifications outlined in the Indonesian Mining Regulation (UU. MINERBA) No. 4 of 2009 on the ban on raw mineral exports, is expected to be the solution to encourage the domestic processing of rare earth minerals. In order to increase the added value of natural resources, the Government encourages the development of the domestic processing industry. The uses of rare earth metal in terms of their economic values are shown in fig. 1.

![Figure 1. Applications of rare earth metals [8].](image)

Phosphates contained in the rare earth metal minerals are difficult to separate, and this condition has caused some constraints in the purification process of rare earth metals [5,9]. According to the literature of Korea monazite sand baking, processing and refining of rare earth metals in the beginning of the separation of phosphate from minerals by baking process [10].

2. Materials and Methods

2.1. Materials

![Figure 2. Qualitative analysis of raw materials mineral.](image)

In this work, the raw sand material obtained as the side products or derivatives of Bangka-Belitung Island tin industrial processing is used as raw material. Minerals contained in the raw material are shown in figure 2. Results of qualitative analysis using X-Ray Diffraction method, indicates that the raw material is dominated by the xenotime mineral. The xenotime mineral fractional content is at least 55% in a 6.0273 gram sample, while the monazite mineral fractional content is 30%. In this research, there are 4 particle size variations. The first variation is -50 100 mesh which is a direct result of the classification of mineral raw materials. The second variation of the particle size of -100+120, the third of -120+170 and the fourth of -200 mesh.
2.2. Methods

The decomposition of phosphate in Korean monazite using NaOH have been carried out by other authors and it is a well proven method and has been used as a reference in comparative literature [8]. Under these same conditions, for the Indonesian raw mineral materials, the authors have examined the effects of temperature and have conducted classification of particle size of the mineral towards phosphate decomposition process using NaOH. The baking process of the raw sand materials was performed at different temperatures (350°C, 400°C, 450°C and 500°C) using a muffle furnace for 120 minutes. After the baking process for a certain period of time, the samples were taken out from the furnace. The mass of sample resulting from the baking process was then leached in hot distilled water (80°C) [10-14] using a magnetic stirrer of 300 rpm (constant agitation) for 60 minutes to dissolve the phosphate ions in the solution. The filtered slurry was dried at 1000°C in order to yield rare earth hydroxide. The experimental method is shown in figure 3.

![Diagram of the experimental method](image)

**Figure 3.** Experimental methods design.

3. Results and Discussion

The main purpose of the baking process is phosphate separation from mineral by decomposition [10]. The effect of particle size and baking temperature on baking process using NaOH was studied. The reaction of mineral decomposition as follow:[1,15]

\[
\text{REPO}_4 + 3\text{NaOH} \rightarrow \text{RE(OH)}_3 + \text{Na}_3\text{PO}_4
\]

Where RE : Rare Earth

Decomposition process of phosphate from mineral is based on the result of baking Korean monazite. Table 1 show the composition of oxide in the raw material used in the experiment.
### Table 1. Raw materials minerals oxide content.

| Compound     | (%)  |
|--------------|------|
| P$_2$O$_5$   | 11.01|
| La$_2$O$_3$  | 6.51 |
| CeO$_2$      | 16.11|
| Nd$_2$O$_3$  | 6.51 |
| Y$_2$O$_3$   | 13.44|
| Pr$_6$O$_{11}$ | 1.18 |
| Er$_2$O$_3$  | 1.12 |
| Dy$_2$O$_3$  | 1.67 |
| Yb$_2$O$_3$  | 1.43 |
| Gd$_2$O$_3$  | 1.04 |
| ThO$_2$      | 4.36 |
| U$_3$O$_8$   | 0.32 |

3.1. Phosphate Decomposition

The washing process of materials produced from baking was carried out using hot distilled water at 80°C. It is based on NaPO$_4$ solubility in H$_2$O. The concentration of phosphate produced from baking process (decomposition) was measured using high pressure liquid chromatography (HPLC). Figure 4 (a) shows the percentage of phosphate produced from baking process with a 200 mesh particle size and a temperature variation. Figure 4 (a) shows the percentage of phosphate decomposition resulting from the baking process of raw material containing 11.01% of P$_2$O$_5$. Figure 4 shows that the optimum condition of baking process for the 200 mesh-particle size classification is to be found at the 400°C baking temperature. The values of the decomposing fraction of phosphate (percentage value) and the energy consumption are the basis for selecting the optimum temperature. At a temperature of 500°C decomposition of phosphate reached 92.96%, meanwhile, at a temperature of 400°C decomposition of phosphate reached 91.40%. The difference of decomposition fraction between the temperature of 400°C and 500°C is only 1.56%, while the energy requirements to reach a temperature of 500°C is greater than the temperature of 400°C. In Figure 4 it is shown that at 450°C there is an anomaly, in which there is a decrease in the fraction of decomposed phosphate while theoretically the decomposition fraction should increase, as it is proportional to the increasing temperature. Figure 4 (b) shows effect of particle size was with respect to the generated decomposition fraction. The smaller particle size is related to lower fraction of phosphate decomposition. In Figure 4 (b), it is shown that maximum decomposition fraction from the 200 mesh particle size is 91.40%. While the lowest phosphate decomposition fraction with the biggest particle size (-50+ 100mesh) is 74.10%. This occurs because one of the factors that support the reaction rate is the cross-sectional area. Therefore, the temperature of 400°C and the 200 mesh-particle size are set to be the optimum decomposition parameters for phosphates. The qualitative manner with which one could prove that the phosphate has completely decomposed is through the results of an x-ray diffraction analysis, as is shown in figure 5. In figure 5 it can be seen that the quantitative results of XRD seems to demonstrate that phosphate (P$_2$O$_5$) has been separated. Comparing the two figures, Figure 6 (a) and (b), there is the undetectable phosphate compound bonding with rare earth elements, and the compounds detected based on the results of the analysis are in fact rare earth oxides.
3.2. Thermodynamic and Kinetic Analysis

Thermodynamic data or parameters such as Gibbs energy, enthalpy and entropy, in relation to the lanthanide (REM) formation reaction process and which is illustrated through the Ellingham diagram is not available at this time. Because Gibbs energy plays a predominant role in the determination of the metallurgical process reaction with the study of thermodynamic aspects, and therefore requiring a more in-depth study to reveal the thermodynamics aspects involved in the baking process of the monazite sand decomposition. Study reinforces the theory of thermodynamics aspects according the reference journals as well as several other clams journals. Based on the reference journal lanthanide hydroxide obtained by the reaction formation as follows:

\[ \text{Lantanida (OH)}^{2+} + 2\text{OH} \rightarrow \text{Lantanida (OH)}_3 \] [11]

On the literature gibbs acquired energy data is unavailable for the formation of all the elements contained in monazite sand or phosphate minerals. Lanthanide elements are accumulated based on research data of the literature is only La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y while the elements of U and Th energy data gibbs formation of hydroxides not available. Assuming the calculations based on data obtained from the literature and that the raw materials minerals are
assumed to contain lanthanide series elements, the equation corresponding to the Gibbs energy in the lanthanide hydroxide formation implies that the reaction can take place spontaneously. Lanthanide element contained in the mineral monazite is the main element in the mineral, and there are 18 elements altogether in the sample, however in the available literature mentions only 15 elements. Based on the similarity of the nature of the lanthanide elements obtained through the calculation of dominant elements Ce in raw materials mineral (according to the composition analysis results) includes the following [11-13]:

\[
\text{Ce(OH)}^{2+} + \text{OH}^- \rightarrow \text{Ce(OH)}_3^3\quad \Delta G_{o}^{298} = -1296.91 \text{ kJ/mol}
\]

\[
3\text{NaOH(s)} \rightarrow \text{Na}_3^+ + \text{OH}^{1-} \quad \Delta G_{o}^{298} = 379.4 \times 3 = +1138.2 \text{ kJ/mol}
\]

\[
\text{Na}_3^+ + \text{PO}_4^{3-} \rightarrow \text{Na}_3\text{PO}_4(s) \quad \Delta G_{o}^{298} = -1819 \text{ kJ/mol}
\]

\[
\text{Ce} + \text{PO}_4^{3-} + 3\text{NaOH(s)} \rightarrow \text{Ce(OH)}_3 + \text{Na}_3\text{PO}_4(s) \quad \Delta G_{o}^{298} = -1977.71 \text{ kJ/mol}
\]

Based on the calculated Ce formation data \( \Delta G_{o}^{298} \), the formation of lanthanides with NaOH and NaPO_4 reactions with NaOH mineral, as the raw starting material, the results thermodynamic analysis shows that this is a spontaneous reaction (\( \Delta G_{o}^{298} < 0 \)). From these calculations are not done thoroughly formation of lanthanide compounds due to the similarity of the nature of the lanthanide spontaneous reactions can already be assumed that \( \Delta G_{o}^{298} < 0 \) on the baking process raw material mineral decomposition using NaOH.

Kinetics metallurgy is one of the factors the length of time or the speed of reaction of a reaction mechanism. Bases the determination of the reaction rate calculation is based on the data percent decomposed. Mechanical rate control equation be an expressed as follows [14-17]:

\[
1 - \left(1 - X \right)^{\frac{2}{3}} = \frac{2mDc}{\beta r_0^2 p} xt \quad (1)
\]

\[
1 - \left(1 - X \right)^{\frac{1}{3}} = \frac{k_c}{r_{0,p}} \cdot t \quad (2)
\]

To predict the baking reaction mechanisms controlling the rate of decomposition, percent decomposition substituted at 1 equations and 2. The results obtained from the equation and the data obtained is then plotted a graph. Data from the equation results have been obtained and classified in table 2.

| Table 2. Calculation Data Results Control Rate Reaction Based Phosphate Decomposition. |
|---------------------------------|---------------------------------|------------------------|
| Description | Rate Control | |
| Clasiffication Size Particle (mesh) | Chemical Reaction | Difussion Control |
| -50 +100 | 1-(1-X)\(^{\frac{2}{3}}\) | 1-(1-X)\(^{\frac{2}{3}}\) |
| -100+120 | 1.873 | 0.873 |
| -120+170 | 1.898 | 0.899 |
| -200 | 1.942 | 0.942 |
Based on figure 6 can be seen in the graph of temperature variations influence on the classification particle size -200 # based rate equation control chemical reactions or diffusion mechanism. The data in figure 6 has show a value of $R^2 = 0.9822$ and $R^2 = 0.9821$, if seen from the amount of $R^2$, the biggest determining the nominal control of there action is diffusion, although the amount of $R^2$ not much different. While the temperature variation or the rate of temperature change is controlled by diffusion and chemical reactions or can be assumed intermediates because of the similarity of regression coefficients.

### 4. Conclusions

The process of baking phosphate decomposition using solid NaOH is the stage of pre-treatment in mineral processing for the purpose of decomposing phosphate contained. On the baking process percent decompose phosphate contained optimum at the particle size classification -200 mesh and temperature of 400ºC which is 91.40%. The particle size is very influential visible from experimental data on the classification of the biggest particle size -50+100 mesh phosphate decomposes 74.10% at a temperature of 400ºC. Temperature also plays an important role in the decomposition of phosphate, the higher the temperature the greater the percentage of phosphate decomposes at temperatures of 500ºC seen in the classification of particle size 200 mesh decompose phosphate highest 92.96%. The mechanism process of baking decomposition reaction is through determination of thermodynamic reaction obtained $\Delta G_m^{298}<0$, so that the reaction takes place spontaneously. Factors supporting the kinetics of the process after a reaction known as spontaneous, gained control in the reaction intermediates based on differences in R2 that is not too high values.

### Acknowledgements

We would like to thank to Tri Purwanti for their hard working on the experimental research and to Center for Accelerator Science and Technology BATAN for financial support.

### References

[1]. Archana K, Rekha P, Manis K J, Jin Y L, Kumar J R, Kumar V 2014 Thermal treatment for the separation of phosphate and recovery of rare earth metals (REMs) from Korean monazite Journal of Industrial and Engineering Chemistry Published by Elsevier BV on behalf of The Korean Society of Industrial and Engineering Chemistry

[2]. Habashi F 2013 Extractive Metallurgy of Rare Earth The Canadian Journal of Metallurgy and Materials Science 52 3
[3]. Gupta C K and Krishnamurthy N 2005 Extractive metallurgy of rare earths CRC Press ISBN 0-415-33340-7

[4]. Gupta A and Yan S D 2006 Mineral Processing Design And Operation Perth Australiae Book ISBN9780080454610

[5]. Haxel G, Hedrick J and Orris J 2012 Rare Earth Elements Critical Resources for High Technology Reston (VA): United States Geological Survey USGS Fact Sheet 087-02

[6]. Lucas J 2015 Rare Earths Purification, Separation, Precipitation and Calcination, Science, Technology Production and Use Pages 69–91

[7]. Chrikst D E, Lobacheva O L and Berlinskii V 2010 Russian Journal of Physical Chemistry A 84 12 2047-2050

[8]. Pecht, Michael G, Robert K E, Song Xin 2012 Rare Earth Materials Insight and Concerns Center for Energetic Concepts Development CALCE Espe Press University of Maryland College Park Maryland USA

[9]. Rekha P and Archana K 2014 J. of Industrial and Engineering Chemistry 2 2035-2042

[10]. Kumari A, Ret P 2014 Thermal treatment for the separation of phosphate and recovery rare earth metals (REMs) from Korean MonaziteJournal of Industrial and Engineering Chemistry XXX

[11]. Chrikst D E, Lobacheva O L and Berlinskii V 2010 Gibbs Energies of Formation of Hydroxides of Lanthanides and Yttrium ISSN 00360244 Russian Journal of Physical Chemistry A 84 12 2047–2050

[12]. Husein H B, Mulyasih Y and Anggraeni A 2011 Extraction and chromatographic studies on rare-earth elements (REEs) from their minerals: the prospect of REEs production in Indonesia Proceedings of the 2nd International Seminar on Chemistry 2011 421-430

[13]. Onyedika G, Christopher O N, Ayebatonworio O and Martin O 2013 Comparative Kinetics of Iron Ore Dissolution in Aqueous HCl-HNO3 System Journal of Minerals and Materials Characterization and Engineering 1 153-159

[14]. Renata D, Abreu, Morais C A 2010 Purification of Rare Earth Elements from Monazite Sulphuric Acid Leach Liquor and The Production of High-Purity Ceric Oxide Minerals Engineering 23 538 – 540.

[15]. Habashi F 2013 Extractive metallurgy of rare earths Canadian Metallurgical Quarterly 2013 52 3.

[16]. Onyedika G O, Christopher N, Ayebatonworio O and Martin O 2013 Comparative Kinetics of Iron Ore Dissolution in Aqueous HCl-HNO3 System Journal of Minerals and Materials Characterization and Engineering 1153-159

[17]. Gharabaghi M, Irannajadband M, Azadmehr A R 2013 Leaching kinetics of nickel extraction from hazardous waste by sulphuric acid and optimization dissolution conditions, chemical engineering research and design 91 325–331.