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MGEI GEOMETALLURGY CONVENTION 2017 (MGC 2017) Hyatt Hotel, Jogjakarta, November 1 – 2, 2017

Hydrometallurgy Process on Radioactive and Rare Earth Elements Extraction from Monazite

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Abstract

Tin mining activities resulting tailing instead of tin metal. Monazite, one of the tailing minerals, contains valuable and strategic elements, such as Rare Earth Elements (REEs), uranium, and thorium. BATAN has developed the extraction methods for those elements. The process stages consist of milling, alkaline leaching, selective dissolution, and multistage precipitation. The products obtained were sodium tri-phosphate, REEs hydroxides, and uranium-thorium hydroxides concentrate. The process technology already brought to pilot scale with 50 kg monazite/batch of capacity.

Keyword: monazite, uranium, thorium, rare earth, extraction

Abstrak

Aktivitas penambangan timah menghasilkan logam timah serta tailing. Salah satu tailing tersebut adalah monasit yang mengandung unsur-unsur strategis dan berharga seperti logam tanah jarang (LTJ), uranium dan torium. BATAN telah menguasai teknologi ekstraksi unsur-unsur tersebut melalui tahapan proses milling, pelindian basa, pelarutan parsial, dan pengendapan bertingkat. Produk yang diperoleh antara lain natrium fosfat, LTJ hidroksida, dan konsentrat uranium-torium hidroksida. Teknologi proses ini telah dikembangkan ke skala pilot dengan kapasitas pengolahan 50 kg monasit/ batch.

Kata kunci: monazite, uranium, torium, logam tanah jarang, ekstraksi

Introduction

Tin production using a pyrometallurgy process requires concentrated cassiterite mineral (SnO₂) as a feed for smelting process. From mining, the ore was processed with several physical process stages, such as jig, magnetic separator, high tension separation, and air table to remove the impurities minerals. The concentration process also results in concentrated impurities that are zircon, xenotime, monazite, and ilmenite instead of cassiterite. This tailing of tin mining activities should be processed further to increase its economic value. In line with national program of Rare Earth Elements (REEs) industrialization in Indonesia, some institutions have collaborated to take part in research for extracting REEs from its minerals and the utilization of REEs as advance materials for various applications.

The concentrated monazite minerals (high grade) -as showed in Figure 1- could have contained REEs about 60%. Other than REEs, monazite also contains uranium (U)

and thorium (Th) which are radioactive elements. Therefore, the concentrated monazite could be categorized as Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM). Table 1 shows typical composition high grade monazite.

BATAN as a government institution that has a responsibility to manage radioactive materials in Indonesia, has developed the process technology for U and Th removal from monazite. The technology is not only produce U and Th concentrate, but also tri-sodium phosphate (Na₃PO₄) and Rare Earth Hydroxide (RE(OH)₃).



Figure 1: High grade monazite

| Tal | able 1:Typical composition of high grade monazite (%). | | | | | | | | | |
|-----|--|------------------|--------------------------------|-------------------------------|--------|--|--|--|--|--|
| | U ₃ O ₈ | ThO ₂ | RE ₂ O ₃ | P ₂ O ₅ | Others | | | | | |
| | 0.09 | 3.60 | 44.88 | 13.09 | 38.34 | | | | | |
| | | | | | | | | | | |

Method

The hydrometallurgy process was used to extract U, Th, and REEs from monazite that consists of milling, alkaline leaching, selective dissolution, and multistage precipitation.

Milling

Size of the monazite's particle has to be reduced to give greater surface area, so the reagent would be effectively contacted with the particles. Types of milling equipment that commonly used are rod mill, ball mill, mortar grinder, etc.

Alkaline leaching

The alkaline leaching using sodium hydroxide to dissolve phosphate, and convert monazite from phosphates compound into hydroxides. Phosphate in aqueous phase separated from leaching residue by filtration.

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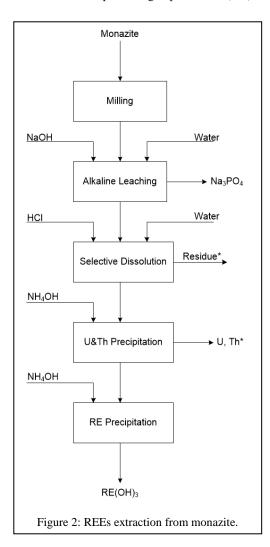
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Selective Dissolution

Leaching residue is reacted with hydrochloric acid in certain pH condition and temperature to dissolve REEs selectively. Selective dissolution is aimed to dissolve REEs with small amount of U and Th as impurities.

Multistage Precipitation

The solution obtained from selective dissolution stage need to be purified, especially to reduce or remove radioactive elements, prior to precipitation of REEs product. Based on the difference of precipitation pH between REEs and U/Th, the multistage precipitation could be used. REEs would be precipitated in higher pH than U/Th. The pH of solution would increase with addition of ammonium hydroxide, and U/Th precipitate should be separated before the precipitation pH of REEs was reached. The REEs hydroxide product could be obtained by continuing the precipitation process into pH 8 – 9.Figure2 shows the flowchart of monazite processing to produce RE(OH)₃.



Result and Discussion

Milling

As required for alkaline leaching stage, milling is aimed to obtain fine size of the monazite. Some studies show that alkaline leaching give satisfying result in -325 mesh of particle size.

Alkaline leaching

Phosphate bond in monazite was broken by sodium hydroxide solution in high temperature, and resulting soluble form of phosphate while U, Th, and REE kept in solid phase as hydroxides. The reaction mechanism as follows:

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REPO<sub>4</sub> + 3NaOH \rightarrow RE(OH)<sub>3</sub>+ Na<sub>3</sub>PO<sub>4</sub>
(UO<sub>2</sub>)<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> + 6NaOH \rightarrow 3UO<sub>2</sub>(OH)<sub>2</sub>+ 2Na<sub>3</sub>PO<sub>4</sub>
Th<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub> + 12 NaOH \rightarrow 3Th(OH)<sub>4</sub>+ 4Na<sub>3</sub>PO<sub>4</sub>
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In this stage, more than 95% phosphate was dissolved. Crystalline phase of phosphate formed at low temperature. Otherwise, the separation of phosphate solution from leaching residue should be brought at high temperature.

Selective Dissolution

REEs contained in leaching residue was dissolved using hydrochloric acid at certain pH and temperature, and resulting REE-chloride solution with small amount of radioactive elements impurities. The reaction mechanism as follows:

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RE(OH)<sub>3</sub> + 3HCl \rightarrowRECl<sub>3</sub>+ 3H<sub>2</sub>O
3 UO<sub>2</sub>(OH)<sub>2</sub> + HCl \rightarrow 3UO<sub>2</sub>Cl<sub>2</sub>+ 3H<sub>2</sub>O
Th(OH)<sub>4</sub> + 4HCl \rightarrowThCl<sub>4</sub>+ 4H<sub>2</sub>O
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Approx. 70% of REEs was dissolved while 5% of U and Th also dissolved into chloride solution.

Multistage Precipitation

Those U and Th should be removed to obtain the RE(OH)₃ product with no radioactive impurities contained. Otherwise, purification of REEs-chloride solution need to be conducted prior to recovery of RE(OH)₃ product.

All radioactive elements were precipitated when pH of REEs-chloride solution increased to neutral pH. The precipitate separated from aqueous phase using filtration method. As a result, the REEs-rich solution was obtained. In latest stage, precipitation of RE(OH)₃ was take place at high pH within atmospheric condition. The reaction of precipitation as follows:

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RECl<sub>3</sub> + 3NH<sub>4</sub>OH \rightarrow RE(OH)<sub>3</sub> + 3NH<sub>4</sub>Cl
UO<sub>2</sub>Cl<sub>2</sub> + 2NH<sub>4</sub>OH \rightarrow UO<sub>2</sub>(OH)<sub>2</sub> + 2NH<sub>4</sub>Cl
ThCl<sub>4</sub> + 4NH<sub>4</sub>OH \rightarrow Th(OH)<sub>4</sub> + 4NH<sub>4</sub>Cl
```

Figure 2 shows the sample of $RE(OH)_3$ product while the composition is provided in Table 2.

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Figure 2: RE(OH)₃ Product

Table 2: Composition of RE(OH)₃ Product (%).

| | Table 2: Composition of RE(OH)3 Product (%). | | | | | | |
|---|--|------------------|--------------------------------|-------------------------------|--------|--|--|
| | U_3O_8 | ThO ₂ | RE ₂ O ₃ | P ₂ O ₅ | Others | | |
| Ī | - | - | 82.65 | 0.02 | 17.33 | | |

The process stages were already developed into pilot scale with 50 kg monazite per batch (Figure 3)in commisioning progress. The pilot plant construction as a base for prefeasibility study before scaling up to commercial/industry. The plant was built in modular system to provide flexibility for future development of the process stages and also enable for processing other radioactive minerals. RE(OH)₃ product result of the pilot plant on progress.



Figure 3: Pilot plant of uranium, thorium, and rare earth elements extraction in BATAN

Conclusion

The hydrometallurgy process which has been developed by BATAN to extract U, Th, and REEs resulting RE(OH)₃ with no radioactive impurities, U-Th hydroxide concentrate, and sodium phosphate as a product. Technology Readiness Level (TRL) of monazite processing to extract U, Th, and REEs should be increased to implementing this technology for commercial scale. Hopefully, this technology could become a trigger for REEs industrialization in Indonesia. For increasing the

added value of RE(OH)3, this REEs concentrate should be separated into oxides of each element. Furthermore, the process technology to utilize REEs as advance material need to be investigated, so the potential of REEs resources would give a maximum benefit for Indonesia.

There are other advantages could be obtained by processing monazite, i.e. monazite as TENORM could be managed properly, reducing the potential of radiation exposure to the society near tin mining area, and increasing the national reserves of energy.

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