Characterization of Malaysian Monazite Concentrate for The Recovery of Thorium Dioxide

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Abstract. Malaysia has many potential mineral resources including some heavy and light rare earth element (HREE and LREE’s) minerals, such as Monazite and Xenotime. Their occurrence is in association with ores containing phosphates and oxides of Cerium (Ce), Lanthanum (La), Neodymium (Nd) and Thorium (Th). Mineralogical characterization of Malaysian Monazite concentrate for the recovery of Thorium dioxide (ThO₂) has been carried out in this study. Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-ray Analyser (EDX) was used to assess the morphology and elemental composition of the mineral. The latter analysis showed that EDX surface analysis detected P-Kα, Th-Mα, La-Lα, Ce-Lα and Nd-Lα as the major elements. The SEM micrographs with the EDX analysis revealed the morphological characteristics of Monazite which showed angled and irregular structures with dark coloured patches of Al, Si and Mn based inclusions. XRF analysis confirmed the presence of Th (8.52 wt.%) and U (0.25 wt.%). XRF also showed that the major rare earth elements (REE) of interest (> 5 wt.%) such as Ce, Nd and La were abundant in the mineral. XRD analysis identified LaPO₄, CePO₄ and NdPO₄ as the major phases. Thorium phosphate (Th₄(PO₄)₄) phase was not detected via XRD due to stronger X-ray reflection from the rare earth phosphates. The information collected from this study will help in developing a suitable process of treatment for the local Monazite, thereby facilitating the mineral to be used a domestic source of Th and other associated REE’s.

1. Introduction

The potential of rare earth elements (REEs) comprising the fifteen elements of the lanthanide series have been recently explored in different applications such as high-strength permanent magnets, catalysts for petroleum refining, metal and glass additives and phosphors used in electronic displays [1]. The solution for a sustainable energy source has gathered widespread attention on minerals that contain Naturally Occurring Radioactive elements namely Monazite and Xenotime in the recent times. Thorium (Th) and uranium (U) represent the heaviest naturally occurring elements on Earth however, the abundance of Th over U in nature is very limited. Added to this, Th is fissile in nature and has replaced U in the nuclear
energy industry as a sustainable and safe alternative [2]. For many years, it has been a tantalizing prospect to use Th as a new primary source of nuclear energy. However, a considerable research and development investment was required to realize the challenge of extracting the latent energy of this element in a cost effective manner [3]. In Malaysia, Th exists in minerals and REE production residue. Malaysia has several minerals (e.g. monazite, zircon, xenotime and ilmenite) which are classified as strategic minerals as it contains a significant amount of Th and U (above 500 ppm) which requires a regulatory control. Malaysian monazite and xenotime minerals contains an average range of about 70,000 and 15,000 ppm respectively. Although Th can become a major radiological problem to our environment if not processed, its prospect as a future alternative fuel in nuclear technology is very promising [4].

Monazite concentrate are found with a variety of other minerals, including silica, magnetite, ilmenite, zircon and garnet [5]. Th is mainly obtained from monazite concentrate as a by-product of extracting rare earth oxides and metals. Although the mineral has a similar combination of elements, they exist with unique mineralogical composition different from another mineral deposit. In this case, a thorough understanding of mineralogy, chemical composition, size, morphology and elemental association with other minerals, by means of in-situ characterization, will provide a basis on the mineral’s behaviour during the separation of the particular REE’s of interest. In this paper, preliminary characterization of the Malaysian monazite concentrate was carried out to understand the morphology, elemental composition and mineral phases present to improve the prospects of using it as a source of Th and other associated REE’s.

2. Materials and Methods

Malaysian Monazite concentrate from Ipoh silica sands were supplied by Ooi Cheng Huat Private Limited. Cone and quartering sampling method was used on the concentrate to have a representative sample for the characterization tests. Polished sections of the samples were prepared using a mixture of epoxy resin and hardener (1:1 ratio) prior to mounting for morphological analyses. The polished sections were coated with Au coating via sputtering for improved conductivity during SEM and mounted. High definition examination of surface morphology and elemental analysis were carried out with a Scanning Electron Microscope equipped with Energy Dispersive X-ray Analyser (Hitachi S-3400N). The identification of mineral phases present in the sample was done using Bruker D8 Advanced X-ray diffractometer. The bulk chemical composition of the mineral was determined by X-ray Fluorescence (XRF) analysis using a Panalytical Axios-Max Spectrometer. The samples were homogenized and hydraulically pressed to form pellets for the XRF analysis.

3. Results and Discussions

3.1 SEM/EDX Analysis

Figures 1 (a)-(b) present the SEM images with EDX analyses taken at specific points of the mineral. The surface morphology showed an angular and irregular shape of the grains due to the weathered nature of the concentrate. The elemental EDX analysis shows that the major elements present are Ce, La, Th, Nd as phosphates. Based on morphological and optical studies in the literature [12], the darker grain in Fig.1(b) indicate traces elements of Al, Si and Mn which exhibit different shades of grey under SEM imaging depending upon their association with other elements in the mineral. The elements of Ce and La in Fig. 1(b) exhibit higher weight concentration which was the characteristic of monazite mineral. Added to this, U can also be observed in trace levels (wt. % < 1) for this micrograph. The high carbon concentration detected was because of the carbon tape in the poly-section. The variations in the elemental combination of the minerals in the SEM/EDX analysis can be attributed to non-uniformity of the texture and particle distribution in the mineral.
Figure 1(a)-(d). SEM/EDX micrographs of Malaysian monazite mineral. Figures 1(c) and (d) correspond to the points marked in SEM micrographs of Figures 1(a) and (b) respectively.
3.2 XRF Analysis

The results of the X-ray Fluorescence Spectroscopy analysis conducted for the monazite was tabulated in Table 1. The analysis indicated that it contained significant amounts of REE elements like Ce, La, Nd and about 8.5 wt.% of Thorium (NORM). Traces of Y, Sm and Gm and Si can also be observed in the mineral with the overall composition below 5 wt.%. A considerable amount Mn of about 8.5 wt.% was present and could be extracted for industrial use in steelmaking [6]. The XRF results show that Th was a chemically bonded along with a wide range of light REE’s which requires distinctive processing and separation techniques. It is due to the presence of numerous elements in the Malaysian monazite mineral which adds to the complexity in separation and recovery of Th. For example, to recover Th, the phosphates composition should be digested [7, 8] or desphosphorized [9, 10].

Table 1. Bulk chemical composition of Malaysian monazite mineral by XRF

| Composition | Content (wt.%) | Composition | Content (wt.%) |
|-------------|---------------|-------------|---------------|
| Al₂O₃       | 0.94          | SnO₂        | 0.301         |
| SiO₂        | 2.56          | La₂O₃       | 11.569        |
| P₂O₅        | 19.391        | CeO₂        | 21.528        |
| SO₃         | 0.118         | Pr₂O₃       | 2.797         |
| K₂O         | 0.056         | Nd₂O₃       | 10.634        |
| CaO         | 0.782         | Sm₂O₃       | 1.756         |
| TiO₂        | 0.267         | Gd₂O₃       | 1.276         |
| MnO         | 8.585         | ThO₂        | 8.525         |
| Fe₂O₃       | 0.529         | U           | 0.253         |
| Y₂O₃        | 1.718         | Others      | ~5.65         |
| ZrO₂        | 0.764         |             |               |

3.3 X-ray diffraction (XRD) Analysis

The elements of Th and REOs usually exist together as they have similar atomic radii [1, 11]. As the monazite bearing of the rare earths was fine in terms of grain size, their identification cannot be done by visual inspection. XRD analysis is an important technique in identifying the mineral phases present in monazite wherein there were chances for multiple phases of the elements to be present in co-existence with the other REE’s. From XRF analysis and literature review, Malaysian monazite comprises of phosphates of Ce, La, Nd, Th predominantly and lesser amounts of Mn, Y, Sm, Gd, Al, Si based compounds [12, 13]. The diffraction pattern of the bulk sample was shown in Figure 2. Phases of LaPO₄, CePO₄ and NdPO₄ are very prominent and are assumed to be present together as their peaks are overlapping with each other [14]. It can be noticed that the analysis identifies CePO₄ in almost every peak because the composition of the mineral is dominated with Ce. However, thorium phosphate is not identified in the diffraction peaks which could be due to the stronger reflection of the X-ray due to the heavy atomic nucleus of Thorium.
Figure 2. X-ray diffractogram of powder monazite.

It is quite interesting to note that a lot of elements identified in the elemental and bulk analysis like Si, Al, Mn, have not been detected by the XRD analysis. One reason is that the mineral was pre-concentrated such that a lot of impurities have been removed at an earlier stage. Also, the intensity of reflected XRD from the rare earths is very high compared to that of the energy of the reflected rays from the lighter elements which makes their detection difficult. Some of the peak positions and their intensities may vary somewhat for specimens of an individual mineral collected from different localities [15]. These differences are due mainly to variations in the elemental content of a particular mineral. It is also possible to identify the minor phases in the mineral, however, it requires partitioning of the diffraction pattern into multiple figures and analysing the figures separately corresponding to one particular mineral and its related phases.

4. Conclusion

The mineralogical characterization on a preliminary level was carried out for Malaysian monazite in this study. The morphological and elemental analysis confirm the presence of Thorium in the concentrate indicating the potential of Malaysian monazite as a source of Thorium. The various REE phosphates (Ce, La, Nd, Pr) present in the mineral were identified by diffraction studies and their composition was determined by X-ray Fluorescence spectroscopy. The knowledge on the mineralogy of Malaysian monazite can be applied to study and improve the available methods of separation for the REE’s and increase the production efficiency of Thorium. Further characterization studies will aid in understanding the chemistry of the composing elements, and will be helpful to propose specialized selective extraction techniques based on the element of interest.

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