

Characterization of Rare Earth Elements at Tailing of Ex-Tin Mining Sands of Singkep Island, Indonesia

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Received : October 07, 2017

Accepted : August 14, 2018

Online : August 31, 2018

Abstract - The objective of this research is to determine the rare earth elements (REEs) from themonazite minerals content of several tin tailing sands (TTS) of ex-tin mining area in Kuala Raya Singkep Island, Indonesia. We used the energy dispersive analysis of X-ray (EDAX)-scanning electron microscopy (SEM) and x-ray diffraction (XRD) to characterize the contents of the samples. The coupled analytical of XRD with SEM/EDX approach enabled to be used for mineralogical identification on the heavy mineral as a rapid determination approach. The analysis of the samples indicates only the presence of REEs including lanthanum (La), cerium (Ce), and thorium (Th) are consistent with the identification of monazite and minerals in the tailing sand. The results show that the average REEs consist of La at 0.2 %, Ce at 7.8 %, and Th at 2.0% respectively. It is concluded that monazite minerals in TTS has an economic potential to be developed. These monazite minerals can be used as material for semiconductor devices.

Keywords: tin tailing sand, rare earth element, XRD, EDAX, SE

Introduction

Tin mining activities on Singkep Island have been started since 1812 (Wing-Easton *et al.*, 1937). In addition to generating foreign exchange for the State, tin mining activities also cause extensive environmental damage. About 4.5 km² of former tin mining concessions has turned into a critical land in the form of tin tailing sand. The acidity and high heavy metal content in the tailings has caused the critical land tin mining to be less productive for agricultural practices.

After stopping tin mining activities in 1993, from 1812 to 1993 most TTS remains were dumped directly into the urban area environment (Firdaus, 2002). Nowadays, there are no longer mining activities that affect the social, economic and environment for the community. These environmental impacts identified in the land after mining is also changing where many pools have been left filled with water almost resembles a lake that has the potential for erosion. Another potentially disruptive impact of environmental quality is the emergence of water waste becomes acidic.

Barnes and Seward (1997) have shown that ex-ore mining is burdened with geogenic, but even more by anthropogenic mercury pollution. Besides soil pollution by atmospherically derived mercury (Hg⁰), considerable amounts of mercury-bearing ore residues were spilled into the environment (Bavec & Gozar, 2012). Concentrations of 42 trace elements, including rare earth, in Croatian thermal waters were investigated (Fiket *et al.* 2015). In nature, there are rare metal deposits that have chemical and physical properties. The REEs are a group of 17 chemically similar metallic elements (15 lanthanides, plus scandium and yttrium). This is due to their essential role in permanent magnets, lamp phosphors, NiHM batteries, catalysts and other applications (Binnemans *et al.*, 2013). Physically, in general form the structure of the metals is the same; this is the reason why alloys of these metals can be found together in nature. Sediment

land composite is a mineral monazite and xenotime high enough (Deer *et al.*, 1997). The REEs, also known as lanthanides, comprise 15 elements with atomic numbers ranging between 57 and 71, that is, from Lanthanum (La) to Lutetium (Lu). The REEs deposits were found in five continents, i.e. Asia, Europe, Australia, North, and South America, and Africa. A total of 34 countries has found REEs deposits. China and Brazil are among the countries with highest production of rare earth minerals deposit (Chen, 2011).

Currently, a growing interest has been given to the rare earth phosphates $REPO_4$. Synthetic $REPO_4$ compounds are commonly named after their natural mineral analog, i.e., monazite for $RE = La$ to Gd or xenotime for $RE = Tb$ to Lu and Y (Bregiroux *et al.*, 2006). The first series has a monoclinic crystalline structure, while the second has a tetragonal crystalline structure (Hezel & Ross, 1967). Alloys of cerium oxide (cerium oxide compounds) have economic value and have been manufactured using the fractionation process results in the number of tons in quantity.

It has been reported determination heavy minerals an ex-tin mining area in Malaysia (Hamzah *et al.*, 2009); it is rich in heavy minerals containing rare earth elements. Researchers have been conducted for separation process of REEs from minerals monazite and xenotime by using the flotation separation technique (Chehreh *et al.*, 2015). The combination of scanning electron microscope (SEM) and energy dispersive analysis by X-ray (EDAX) are used for nondestructive qualitative and quantitative elemental analysis of individual particles at micron level as well as for analysis of their morphology (Miler & Gosar, 2012). The characterization of the composition and morphology of the various phases that have valuable rare earth elements in the ores are needed in conjunction with the study of their physicochemical properties to optimize the industrial process for extracting the minerals (Demers *et al.*, 2013). Similar studies have been conducted by Irzon *et al.*, (2014) based on the geological map of Singkep in the south and southwest where the total content REEs is 3302.67 ppm which is determined by using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Our present study was to determine REEs content from monazite minerals by using SEM/EDAX. The qualitative, morphology and structural analysis of samples were presented in this paper.

Materials and Methods

The study area is located in the northern part of the Singkep Island (Figure 1), geographically situated between $103^{\circ}30' - 105^{\circ}00'$ E dan $0^{\circ}00' - 1^{\circ}00'$ S (black color on the map of Figure 2). This map was constructed after modified by Irzon *et al.*, (2014) to indicate the sampling location (black box of figure 2).



Figure 1 Map of study area in Singkep Island.

We collected complete TTS samples connected to the sand four sampling stations at Kuala Raya using hand auger. The selection of the sampling point was based on the assumption that REEs content is deposited on

the sites close to ex-tin mines over time. A total of 4 TTS samples were collected from several locations at Kuala Raya as shown in figure 2.

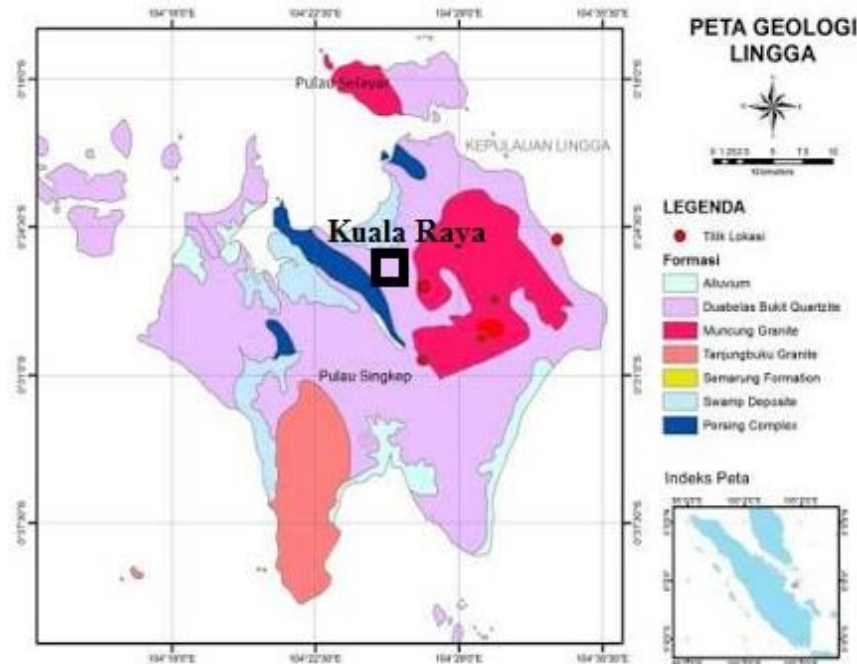


Figure 2 Ex-tin mining sands at Kuala Raya village, Singkep Island (modified from Irzon *et al*, 2014).

All the sample were labeled as S1, S2, S3, and S4 and kept in black poly bags and then sent to the laboratory for analysis. The next step, the samples were washed with water and was kept for an hour in a container after washing with water, leaving behind the dense material. Specimen were then dried in an oven at 70°C (Mohanty *et al.*, 2003). Finally, the specimens graded into homogeneous granules by using Matest Auto Sieve Shaker. The sample region is dominated by old quaternary alluvial deposits consisting of sand, gravel measuring 0.5-10 cm. The granule size of 250µm and the sand concentrates were then separated into different fractions for analysis using SEM/EDAX and XRD.

The composition of the film was determined by energy dispersive analysis by X-rays (EDAX) on 2 or more areas of each grain to minimize errors. The EDAX system attached to a scanning electron microscope (SEM) (JEOL JXA-8900) for morphological examinations of mineral grains. The samples were coated using gold (thermal evaporation) for 60 seconds to ensure that the sample as conductive stage before undergoes grain analysis. The structural phases were identified from powder diffraction files (PDF) of the International Center for Diffraction Data (ICDD).

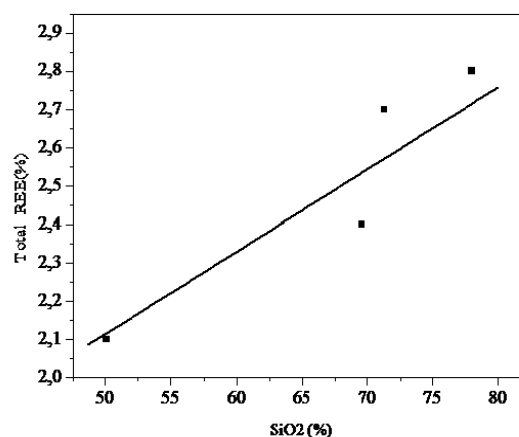
Results and Discussions

The elemental content in atomic percent (at.%) for TTS being analyzed (Table-1). The samples in the study area containing 7 elements weredeterminate and then classified according to major elements (Si, Pt, Al, Fe and Hg), rear earth elements (Ce, La, and Th). From the measurement results EDAX identified some major elements such as Si, Pt, Al, and Fe are found to be observed from all samples. The content of Si in the range of 50.1 ~ 78.0 % in samples, the highest of which sample S1, was about 1.2 times the sample S4. The results show that the tin tailing sand was 5 major elements content. The content of major elements Si > Hg > Al > Pt > Fe, and the average contents of 5 element of metals were 67.25%, 30.00%, 12.22%, 8.38% and 2.15% respectively.

Table 1. The elemental content of TTS sample (at.%).

| Element (spect.line) | Sample S1 | Sample S2 | Sample S3 | Sample S4 |
|-------------------------|-----------|-----------|-----------|-----------|
| Si-K α | 78.0 | 71.3 | 69.6 | 50.1 |
| Pt-M α | 7.7 | 6.1 | 8.2 | 11.5 |
| Al-K α | 9.5 | 15.3 | 19.0 | 5.1 |
| Fe K α | 2.0 | 4.6 | 0.8 | 1.2 |
| Hg-M α | nd | nd | nd | 30.0 |
| Ce-L α | 2.2 | 2.0 | 2.1 | 1.5 |
| La-L α | nd | nd | nd | 0.2 |
| Th-M α | 0.6 | 0.7 | 0.3 | 0.4 |
| Σ REE | 2.8 | 2.7 | 2.4 | 2.1 |

The accumulation content of Si metal in sample decreased with increasing series a sample taken at the study area. In sand tailings, the predominance of coarse materials, mainly sand or quartz particles, therefore all samples contain Si metal. This clearly shows that the sample containing Si as elements forming Silica (SiO₄) in the sand. Besides, identified the dominant element Pt metal on, wherein the content ranged from 6.1 to 7.7%. Another dominant metallic element is Al with a content of 5.1 to 19.0%. In all samples the smallest content of the major element was Fe metal ranged from 0.8 to 4.6%. In the sample S4 identified heavy metals Hg with a content of 30.0% S4 sample is a population of particles containing Hg, Si and also Pt, Al, and Fe as major elements and is ascribed to silicate grains covered with Hg and/or Fe compounds. The Hg-riches assumed to be dominated by HgS polymorphs, which is typical for cinnabar concentrates from heavy mineral tail sands. The Hg probably moves as Hg⁰ in a hydrated aqueous species, possibly with subordinate sulfide complexes (Sroor, 2003). Mercury is known to be transported both by vapor and liquid phases in New Zealand geothermal (Barnes & Seward, 1997). From the table 1, the average mean value of detected in the samples shows that the content of REE (Ce and Th) varied between 0.6 and 2.7% with an average value of 2.07%. The content of the Ce in sample S2, S3, and S4 which relatively similar to the analysis of REEs element in ore concentrate samples using direct current plasma spectrometry (Christenson & Mroczek, 2003). REEs exist in mineral forms in nature, also occurs associated with tin deposits together with rare earth minerals such as monazite and xenotime. Monazite and xenotime are a very dense mineral can be found together in the same area TTS. Monazite content is also found with 1.31 wt.% on raw in Bangka Island Indonesia (Johnson & Sisneros, 1981). In this research, we found two types of monazite and xenotime minerals with the chemical composition of (Ce, La, Th)PO₄. However, figure 3 shows the total REEs minerals versus SiO₂ content data of TTS indicate that monazite is present at four stations originating from weathering of metamorphic bedrock in the tin Singkep island.

Figure 3. Variation of REEs vs SiO₂.

Monazite contain the lowest content of Th in all samples varied between 0.3 to 0.6%. Geochemical studies of monazite sands of Chhatrapur beach placer deposits of Orissa, India show that differentiation of alkali rocks produces Th-poor monazite (Irzon *et al.*, 2014). In many parts of the world, monazite

concentrated in sands is worked as a source of Ce and other REEs. In Egypt, Mohanty reported that the monazite from the black sand deposits may be considered as a source of Ce and La (Mohanty *et al.*, 2003). From these data, it was clear that the former TTson the Singkep Island contains the elements of the rare earth metals although the percentage composition is very small. This is consistent with data reported by Hamzah *et al.* (2009), the mineral monazite contents REEs. The small size of the rare earth element content of metals caused that rare metal content is deposited on the wane by time and weather. This is because the sampling sample is determined by age class how long the mine was abandoned. XRD measurement is needed to be able to determine and analyze the type of REEs structured in a sample clearly.

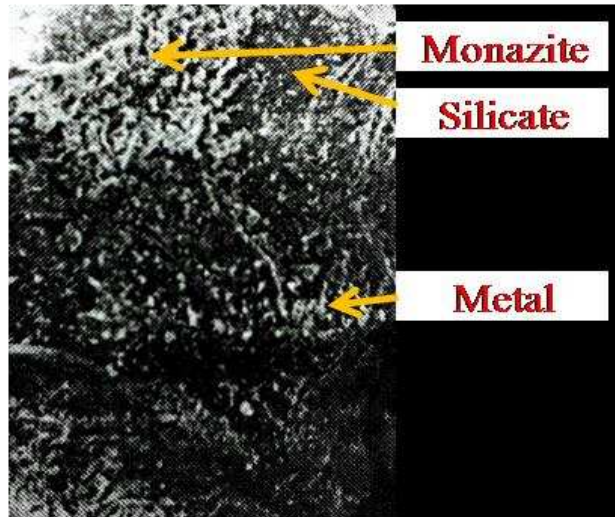


Figure-3. BSE-SEM image of sample S4

A back scattered electron (BSE) image of the S1 sample (Figure 3) revealed that REEs grains often contained inclusions, which SEM analysis (Figure.4) suggests that it may comprise monazite amongst other phases with a population of particles containing Hg, Si and also Fe, Al, and Pt as major elements Ce, La and Th containing minerals, notable monazite was detected but only in small amounts.

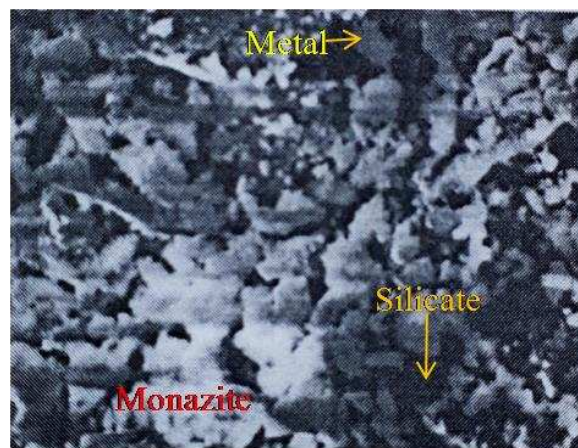


Figure 4 SEM image of surface morphology sample 4.

The identification of the sample was based on a qualitative elemental composition given as average x-ray intensities of the particles of which they were shown in Table. 2. It should be observed that the results are only based on the peak the elements that were detected by XRD measurement.

Table 2 XRD data peak list for S4 sample.

| Element | 2 θ | I (a.u) | d (Å) | hkl | Structure |
|---------|------------|---------|-------|-----|------------|
| Al | 41.5 | 678 | 2.174 | 111 | cubic |
| Si | 53.2 | 6565 | 1.720 | 210 | cubic |
| Hg | 72.9 | 850 | 1.296 | 302 | Tetragonal |
| Pt | 73.1 | 1091 | 1.293 | 220 | cubic |
| Th | 78.8 | 538 | 1.214 | 300 | cubic |
| Ce | 80.6 | 370 | 1.191 | 310 | cubic |
| La | 91.4 | 239 | 1.142 | 222 | cubic |
| Fe | 100.5 | 790 | 1.005 | 321 | cubic |

The present data peak list shows that Al, Si, Hg, Pt, and Fe are present in the sample and were observed by its characteristics (111), (210), (302), (222) and (321) peak with diameter spacing 2.174, 1.720, 1.296, 1.293 and 1.005 Å respectively. The reflections around 1.214, 310 and 222 Å indicated the presence of monazite (Th, Ce, and La) are at the peak list, which possibly corresponds to peak (300), (310) and (222) in Table 2 from the XRD graphic readout. The XRD data peak list for S4 sample further suggests the presence of monazite mineral in the TTS Singkep Island but considering the low content of REEs identified by the EDS analysis. They are only contained in minor quantities when compared to the major element.

Conclusions

It is concluded that the sand samples of Raya ex-mining area in Singkep Island Indonesia contain REEs mineral monazite. The qualitative analysis by SEM/EDS and XRD shows that the monazite mineral containing metals thorium, lanthanum and cerium with the percentage composition is very small. There is also elements of heavy metal Hg which is impurities in the major elements such as silicon, aluminum, platinum, and iron.

Acknowledgements

This research was funded by LPIU DUE-Project University of Riau (IBRD Loan No. 4043-IND) and Directorate of Higher Education of the Republic of Indonesia.

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