

Frontier looking of rare-earth processed residue as sustainable thorium resources: An Insight into chemical composition and separation of thorium

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ABSTRACT

Rare-earth (RE) extraction activities in Malaysia produce an average of 75000 tonnes of Water Leach Purification (WLP) residue containing an estimated 106 tonnes of thorium that leads to negative perception and concern among the public especially related to the environmental and radiological aspects. The main challenge to separate thorium from the WLP residues is the formation of insoluble thorium pyrophosphate (ThP₂O₇) due to the treatment process during rare-earth extraction. Therefore, the objectives of this study are to verify the thorium composition in WLP residue as well as to investigate the possibility of separating thorium from WLP. The characterizations using FTIR, SEM-EDS, XRD, and XPS verified the presence of ThP₂O₇ along with other thorium phosphate compounds (Th(PO₃)₄) and (Th₃(PO₄)₄) in WLP residue. The digestion study using sulphuric acid (H₂SO₄) at various molarity ranging from 3 to 18 mol/L showed that thorium in WLP can be dissolved in acid. The dissolution of thorium up to 50% was achieved at 6 mol/L H₂SO₄ and further increase to 90% with the increase of acid molarity at 150 °C within an hour of the leaching time. This research showed promising findings on the separating thorium from WLP residue through the acid digestion process that might open up the possibility of recycling rare-earth residue as sustainable thorium resources.

1. Introduction

Lynas Advanced Material Plant (LAMP) is the world's largest facility rare-earth processing factory located in Gebeng, Pahang, Malaysia (Phua and Velu, 2012). This facility is designed to treat monazite concentrate also known as lanthanide concentrated (LC), obtained from mining activities in Mount Weld located in Western Australia. Monazite concentrate undergoes a hydrometallurgical process that involves cracking and separation process using concentrated sulphuric acid. Treatment of monazite concentrate finally produces Rare Earths Oxide (REO) products which are then sold globally including Japan, Europe, China, and North America to meet industrial demand. In general, LAMP produces two major by-products as part of REO production which is Neutralization Underflow (NUF) and Water Leach Purification Residue (WLP).

WLP residue is categorized as a radioactive material by the government of Malaysia as the thorium concentration has exceeded the limit of 1000 Bq/kg (Malaysia, 2011). The concentration of thorium in WLP reported by RIA was 6727.64 Bq/kg (Lynas, 2011). Currently, there has been a renewed interest in using thorium as a fuel source in nuclear

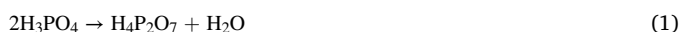
technologies as thorium is found to be more abundant compared to that of uranium (Jordan et al., 2015). Hence, the extraction of thorium from WLP residues produced by the plant assures a promising future for Malaysia.

The accumulated amount of WLP residue generated by rare-earth processing industry from 2012 to 2018 was more than 450000 tonnes, as reported by the Malaysian Ministry of Energy, Science, Technology, Environment and Climate Change (MESTECC, 2018). Taking 6727.64 Bq/kg concentration of thorium reported by RIA, with an equivalent to 1655 mg/kg, thus by taking advantage of thorium in WLP residue, there is about 106 tonnes of thorium that can be potentially recovered annually from WLP residue. Previous study (Jordan et al., 2015) estimated about 94 tonnes of thorium can be recovered every year from Lynas rare-earth processing activity. Recently in Malaysia, the extraction of thorium from industrial waste like monazite using sulphuric acid technology is widely studied. About 2636 tonnes of Malaysian monazite was produced within 5 years (2006–2010) and it was estimated that Malaysian monazite contains about 184.5 tonnes of thorium (AL-Areji et al., 2015). In addition to that, the production of nuclear fuel-grade which are ThO₂ (Bahri et al., 2018; Mohd Salehuddin et al., 2019a,

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2019b) and ThF₄ (Bahri et al., 2019) have been successfully synthesised from local monazite. Therefore, WLP residue has the potential to be one of the thorium sources for Malaysia in the nearest future. A previous study (Balaram, 2019) reported that world REE demand will increase as reflect the new technology requirements that lead to the manifold and vigorous exploration efforts to find new REE ore deposits. Consequently, the increase of REE extraction activities will also generate a huge amount of radioactive residue. If not handled properly, the radioactive residue will be a significant burden to the country, related industries as well as the environment that can cause negative perception and opposition among the public. The radiological risk associated with thorium in the tin processed residue was found to decrease after the separation process was performed (Al-Areqi et al., 2016). In line with that, the recovery of thorium from the residues will provide a sustainable and alternative to the conventional thorium resource, and may improve the acceptance among the public towards the rare-earth industry.

The main challenge when separating thorium from the WLP residues is the formation of thorium pyrophosphate (ThP₂O₇). Rare-earth elements were extracted from monazite concentrate through the process of digestion with concentrated sulphuric acid while simultaneously heating the mixture at the temperature of 650 °C (Schmidt, 2013). At this temperature, ThP₂O₇ is formed instead of thorium sulphate. At high temperatures, phosphate reacts with H₂SO₄ to form H₃PO₄ before dehydrates to form pyrophosphoric acid (H₄P₂O₇). The formation of ThP₂O₇ is given in Eq. (1) and Eq. (2). Previous studies reported that the insoluble ThP₂O₇ will form at the temperature above 230°C (Yemel'yanov and Yevstyukhin, 1969; Qi, 2018), although no experimental evidence for this species was provided (Demol et al., 2018).



The accumulation of WLP residue containing thorium with amounts exceeding the regulatory limit is not something normal that can be easily accepted by the nearby residents as well as the public. On the other hand, disposing of the huge amount of low-level radioactive waste may pose a significant challenge in terms of costs; building a disposal facility might not benefit both industry and country. Therefore, scientific characterization is imperative to reveal the actual composition of thorium in WLP residue to further investigate at thorium separation capability from the residue.

Unlike WLP, the chemical composition and digestion process of waste generated from tin-tailing processing such as monazite is well understood (Bahri et al., 2018; Nurrul et al., 2019; Udayakumar et al., 2020). Since thorium in WLP exists as phosphate compound which is almost identical to monazite ore, the digestion of WLP can be studied by implementing a similar route with different separation parameters (e.g molarity, temperature and leaching time). The utilization of sulphuric acid as digestion medium is due to higher recovery of thorium (Loren et al., 2017, 2018) and lower cost than alkaline digestion technique (Bennett et al., 2020).

The first part of this study is to determine the elemental composition and verified the presence of thorium pyrophosphate in WLP residue by using High Purity of Germanium (HPGe) radiation detector, Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope and Energy-Dispersive Spectroscopy (SEM-EDS), X-ray Photoelectron Spectroscopy (XPS) and The X-ray Diffraction (XRD) techniques. The second part of this study is to investigate the possibility of separating thorium from WLP residue through digestion process by using sulphuric acid. The study was carried out to obtain the optimum parameter in terms of molarity of sulphuric acid (mol/L), digestion temperature (C°), and leaching time (t) to convert thorium compound in WLP into the soluble form of thorium sulphate, thus permitting the extraction of thorium.

2. Material and method

The WLP residue was obtained from Lynas Advanced Material Plant (LAMP) in Gebeng, Pahang Malaysia. The present study followed the standard sample preparation procedure as mentioned in the IAEA technical report series no 295 (IAEA, 1989). Samples were oven-dried for 72 h at 105 °C to ensure significant moisture content was removed. Samples were left to cool at room temperature before grinded and sieved 500 µm-sized mesh to obtain a homogenous powder. The element composition in WLP analysed using Fourier-Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy micrograph and Energy-Dispersive Spectroscopy (SEM-EDS), The X-ray diffraction (XRD) and The X-ray Photoelectron Spectroscopy XPS techniques. Meanwhile, the concentration of uranium (²³⁸U) and thorium (Th²³²) were determined for 12 h of counting time using gamma spectrometry system with a High-purity Germanium (HPGe) radiation detector coupled to a multi-channel analyser.

2.1. Natural radioactivity analysis

The treated WLP residue sample (as mention in 2.0) was packed into an airtight acrylic counting bottle. Before counting, the samples were kept for 30 days to attain secular equilibrium with the parent's radionuclide (U²³⁸ and Th²³²) and their progenies. In secular equilibrium, both parent and progeny activities are equal, and both decay with the half of the parent nuclide. After 30 days, the WLP residue sample was counted for 12 h using a gamma spectrometer system with a High Purity of Germanium Detector (HPGe) to determine the concentrations of the natural radionuclides in the sample. Each sample was prepared, packed and replicated thrice in accordance with the International Atomic Energy Agency (IAEA) guideline (IAEA, 1989). The activity concentrations of U²³⁸ and Th²³² were determined at peak energies of 1764 keV and 2614 keV respectively. The detector was calibrated using the standard source with a mixture of ²²Na, ⁵⁷Co, ⁶⁰Co, and ¹³⁷Cs. HPGe detector (GC3018) was used with a relative efficiency of 30% and a resolution of 1.8 keV at 1.33 MeV and the analysis of photo peaks was performed using Genie-2000 software (Canberra Inc). The detection limit (DL) and minimum detectable activity (MDA) of the detector for energy peak 1764 keV and 2614 keV are (67 ± 0.5 and 86 ± 4 Bq/kg) and (6.2 ± 0.1 and 5.3 ± 0.1 Bq/kg) respectively. IAEA Soil-375 was used as certified reference material in this study. The activity concentration of ²³⁸U and ²³²Th were determined using the equation as reported earlier (Ismail et al., 2018; Shittu Abdullahi et al., 2019a, 2019b).

2.2. Characterization of thorium compound in WLP residue

2.2.1. FTIR analysis

Attenuated total reflectance infrared (ATR-FTIR) spectrometry was used to analyse the chemical composition of the residue surface. FTIR spectrum of WLP was collected using ATR-FTIR (model spectrum 400 FT-IR/NIR) supplied by PerkinElmer with a resolution of 8 cm⁻¹ and wavenumber between 650 cm⁻¹ to 4000 cm⁻¹.

2.2.2. SEM/EDS analysis

Scanning electron microscopy images and energy-dispersive spectroscopy data were recorded on a SEM PHILIPS XL 30 Scanning Electron Microscope with the energy of the electron beam being 30 kV. Samples were mounted directly on the carbon conductive tape with Ag coating.

2.2.3. XRD analysis

The X-ray diffraction (XRD) pattern was recorded on a Bruker XRD D8 advance X-ray diffractometer with a Cu Kα source (λ = 0.1542 nm). The scans were performed at a speed of 0.02°/1.2 s ranging from 2θ = 10–70° at 40 kV and 30 mA. Spectrums were analysed using Diffrac.Eva software.

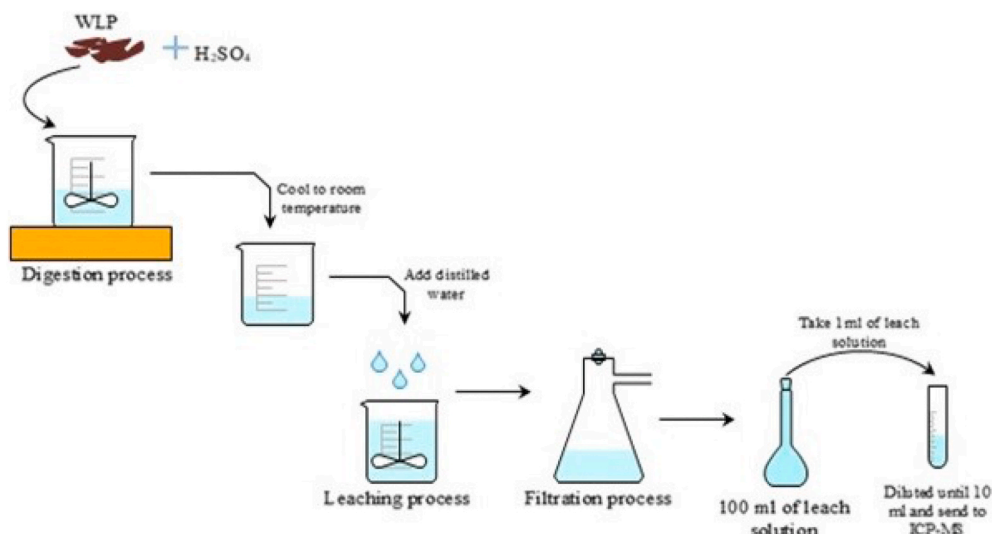


Fig. 1. Schematic diagram of digestion and leaching process of WLP residue.

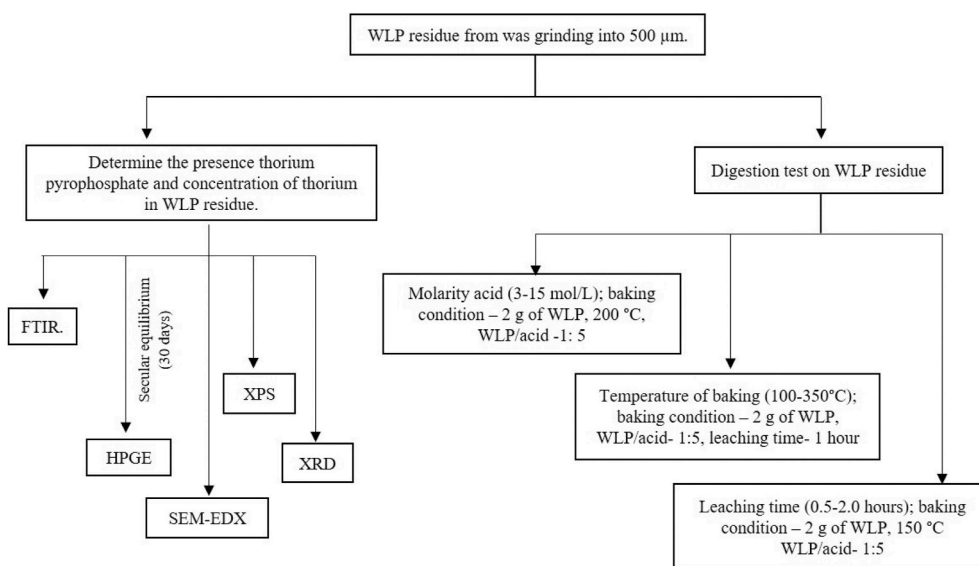


Fig. 2. Experimental scheme for WLP residue.

2.2.4. XPS analysis

The X-ray Photoelectron Spectroscopy (XPS) model Axis Ultra DLD is performed to analyse the chemical bonding, band structure, and elemental composition of the photoelectrodes, using Al Ka x-ray gun.

2.3. Sulphuric acid digestion process

Sulphuric acid digestion was carried out with a sample to the acid ratio (S/A) of 1:5. This wet digestion process was carried out using hotplate for 2 h with constant stirring at 600 rpm as shown in Fig. 1. The 2 h of digestion with the solid to acid ratio of 1:5 was sufficient to reach the maximum dissolution of thorium in sulphate medium (Loren et al., 2017, 2018; Amaral et al., 2018). In this study, an open heating system was used to digest WLP and the evaporation effect of H_2SO_4 towards the digestion process was not further investigated. However, the open heating system using conventional hot-plate with a magnetic stirrer is considered as an establish and widely used technique due to the capability to reach maximum dissolution of thorium during the digestion process. (Demol et al., 2019; Sadri et al., 2017).

After 2 h, the mixture was cooled to room temperature. A similar

volume of distilled water was added to dissolve the metal sulphate, the leaching process happens afterward at room temperature and was then filtered to produce a clear leaching solution. The concentration of thorium and other elements in the leached solution was determined by using ICP-MS. The ICP-MS instrument used was an ELAN 9000 (PerkinElmer SCIEX). A standard solution was prepared using PerkinElmer Pure Plus (multi-element calibration standard 2). Three parameters, molarity, temperature and time of leaching were analysed from the acid digestion process as shown in Fig. 2.

The first parameter tested for different molarity of sulphuric acid (H_2SO_4). 5 different molarity of sulphuric acid were prepared which were 3 mol/L, 9 mol/L, 6 mol/L, 12 mol/L, 15 mol/L and 18 mol/L (concentrated 98% H_2SO_4). The temperature was fixed for 200 °C and leaching time was 0.5 h. The temperature of 200 °C was chosen based on our previous finding regarding monazite digestion, where the best temperature for thorium recovery was between 200 and 230 °C (Bahri et al., 2018).

The effect of temperature was the second parameter tested. To find the best digestion temperature for the WLP residue, concentrated sulphuric acid (98% H_2SO_4) was used. The temperatures tested were 100

Table 1

List of concentrations of NORM in WLP residue by determined in this study compared to others reported.

Technique	Average radionuclide concentration (Bq/kg)		References
	Th ²³²	U ²³⁸	
-	6727.64	271.60	Lynas (2011)
NAA	7938.52	212.35	Balaram (2019)
HPGe-MCA	6229.83	460.54	This study

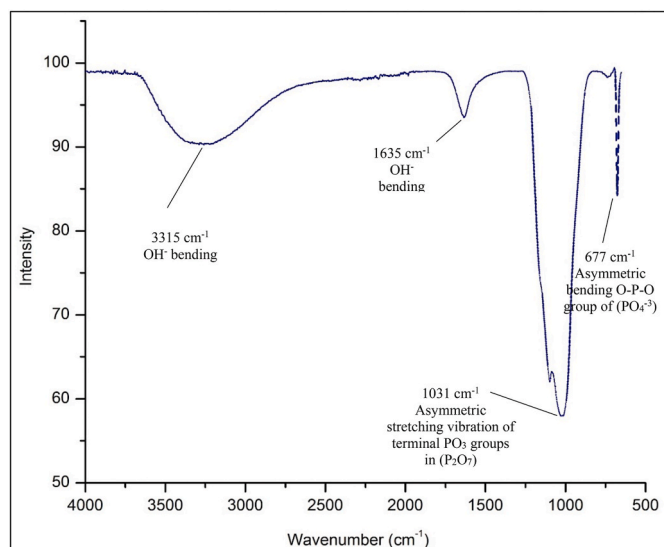


Fig. 3. Pyrophosphate group peak in WLP residue by FTIR analysis.

°C, 150 °C, 200 °C, 250 °C, 300 °C, 350 °C and leaching time is 1 h.

Finally, the third parameter was leaching time, where 0.5 h, 1.0 h, 1.5 h, and 2.0 h leaching times were tested. The temperature was fixed at the optimum temperature (150 °C) for the digestion of WLP obtained from pervious parameter tested. Each sample was prepared in three replicates and the reproducibility of the results were presented in terms of deviation in the data.

3. Result and discussion

3.1. Radioactivity concentrations of ²³²Th and ²³⁸U in WLP residue

Table 1 summarizes and compares the activity concentrations of ²³²Th and ²³⁸U obtained in this research with the other studies. The average activity concentrations of ²³⁸U and ²³²Th were 460.54 ± 37.9 Bq/kg and 6229.8 ± 133.6 Bq/kg, respectively. This value equal to 37.3 mg/kg of uranium and 1532.5 mg/kg of thorium, based on the conversion factor of 1 Bq ²³⁸U/kg = 0.081 mg/kg and 1 Bq ²³²Th/kg = 0.246 mg/kg, respectively. The highest activity concentrations of ²³²Th and ²³⁸U reported were 7938.52 Bq/kg and 460.54 Bq/kg.

3.2. Verification of thorium composition in WLP

3.2.1. FTIR analysis

The FTIR spectrum of WLP is presented in **Fig. 3**. From the FTIR spectrums, there are 3 clear sharp peaks detected in the sample which are 677 cm⁻¹, 1031 cm⁻¹, and 1635 cm⁻¹ while 1 broad peak at 3315 cm⁻¹. A previous study (Jastrzebski et al., 2011) reported the observation of peak between 670 and 500 cm⁻¹ that corresponds to (O-P-O bending) due to (PO₄)³⁻ ions also known as orthophosphate vibrations. In addition to that, the polyphosphate group was detected at the peak between 600 and 400 cm⁻¹ (Deva et al., 2018). Whereas the peak of 631 cm⁻¹ referred to as the asymmetric bending (O-P-O) peak for polyphosphate (PO₃) and orthophosphate (PO₄) (Rachid et al., 2010). Since peak 677 cm⁻¹ in this study is beyond 600 cm⁻¹ and very close to 670 cm⁻¹ peak, thus peak at 677 cm⁻¹ as seen in **Fig. 3** can be referred to as the asymmetric bending O-P-O group of orthophosphate (PO₄)³⁻.

The vibration peak for pyrophosphate (P₂O₇)⁴⁻ group (also written as O₃P-O-PO₃) can be detected between 1249 cm⁻¹ and 412 cm⁻¹ (Deva et al., 2018). Besides that, the peak at 1070 cm⁻¹ is attributed to the asymmetric stretching vibration of terminal PO₃ groups in pyrophosphate (P₂O₇)⁴⁻ (Hirai et al., 2010; Socrates, 2001). The symmetric stretch of PO₃ groups in pyrophosphate (P₂O₇)⁴⁻ was observed at the peak of 920 cm⁻¹ (Ilieva et al., 2001a, 2001b), while the vibration pyrophosphate peak was detected at 1065 cm⁻¹ (Demol et al., 2018). The peak 1031 cm⁻¹ (as shown in **Fig. 3**) is located between 1249 cm⁻¹ and 412 cm⁻¹ which corresponds to the asymmetric stretching vibration terminal PO₃ of pyrophosphate group (P₂O₇)⁴⁻ in WLP sample. The peaks of 1635 cm⁻¹ and 3315 cm⁻¹ indicates the presence of water molecules in WLP.

3.2.2. SEM-EDS analysis

Fig. 4(a) and (b) presents the SEM micrograph and EDS spectra of

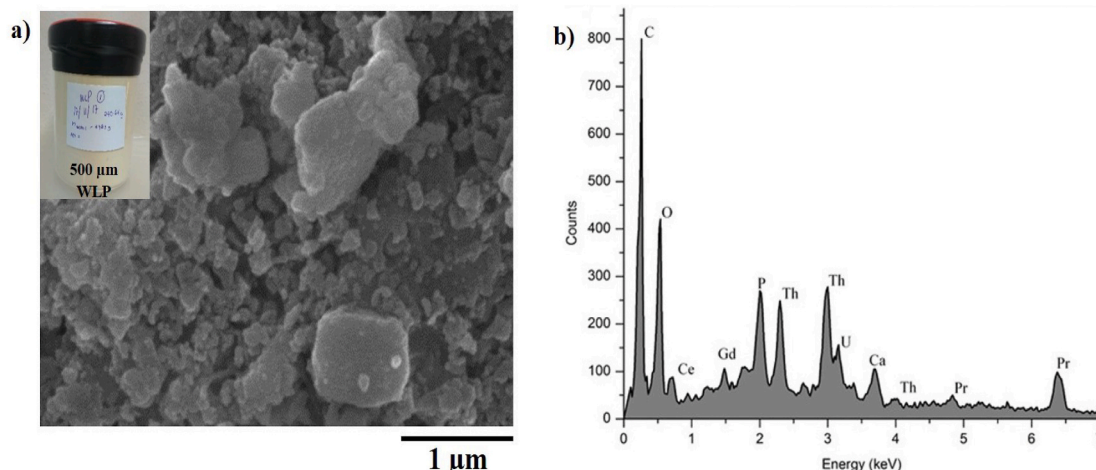


Fig. 4. (a) SEM/EDS WLP residue at low magnification; (b) EDS spectra of WLP.

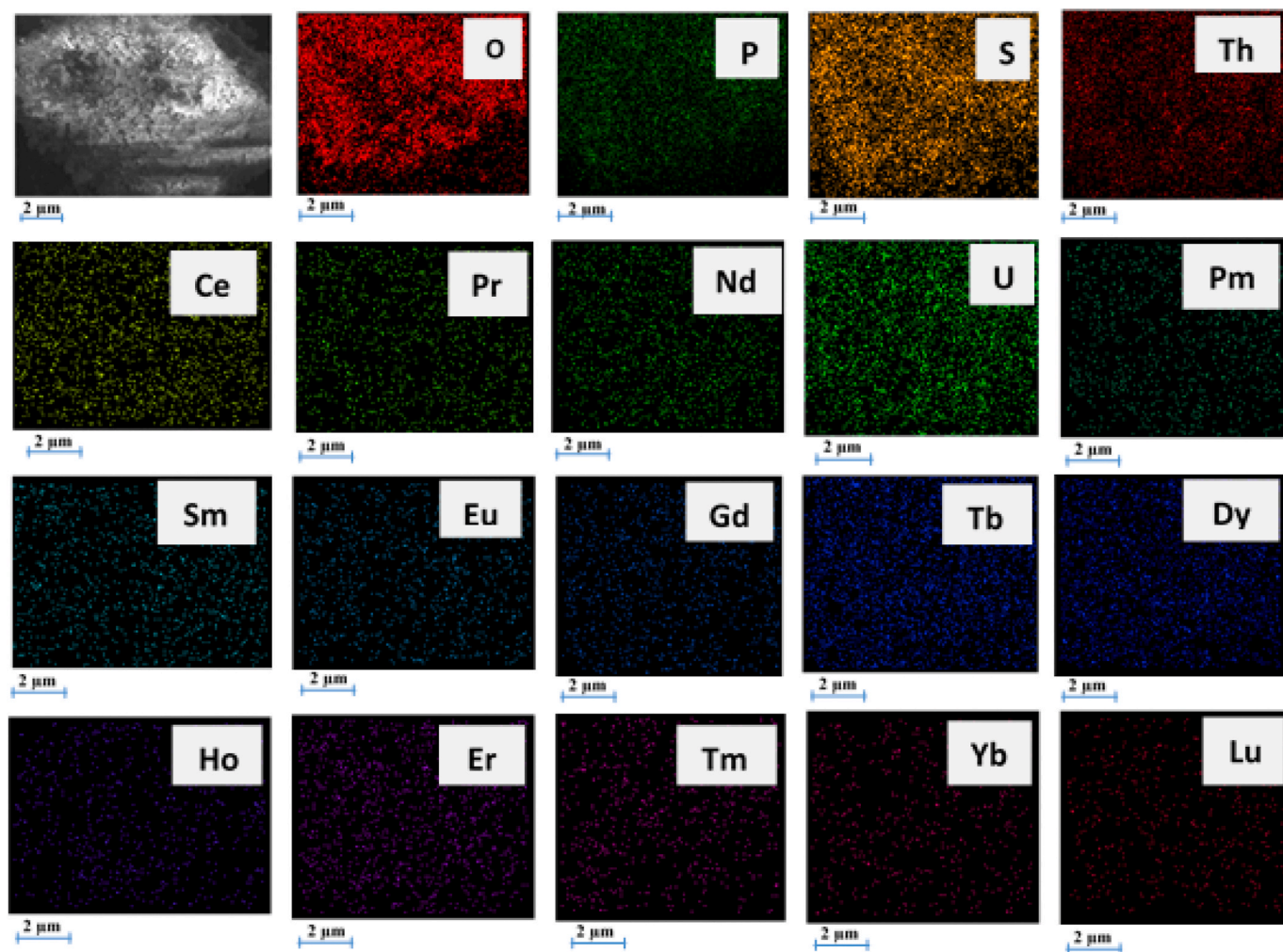


Fig. 5. Element that contains in WLP residue by using EDS mapping.

Table 2
Atomic percentage (%) of EDS measurement for WLP residue.

Point of EDS analysis	Atomic percentage (%)		Ratio Th:P
	Thorium	Phosphate	
1	1.8	8.4	1:4.7
2	4.4	6.0	1:1.4
3	4.1	7.2	1:1.8
4	2.5	9.3	1:3.7
5	3.3	9.3	1:2.8
6	2.0	7.0	1:3.5
Average			1:2.4

WLP residue respectively. The physical properties of WLP residue is in homogenous mixture as shown in Fig. 4(a), while surface morphology analysis using Scanning Electron Microscope (SEM) showed the residue consist of an angular and irregular shape of grains. EDS mapping analysis shows the residue also contains other elements such as REE elements in Fig. 5.

From EDS measurement shown in Table 1, the average atomic percentage based on 6 point EDS measurements, was 3.0% (w/w) Th, 7.8% (w/w) P, 1.3% (w/w) Ce, 0.9% (w/w) Gd and 0.8% (w/w) Eu. The average atomic ratio of Th:P 6 points of EDS is near to 1:2. This ratio indicates the existence of thorium pyrophosphate compound (ThP_2O_7) in WLP residue with the substitution of other rare earth elements. However, Table 2 shows that out of 2 from 6 point EDS measurement shows the atomic ratio thorium to phosphorus is near to 1:4 which

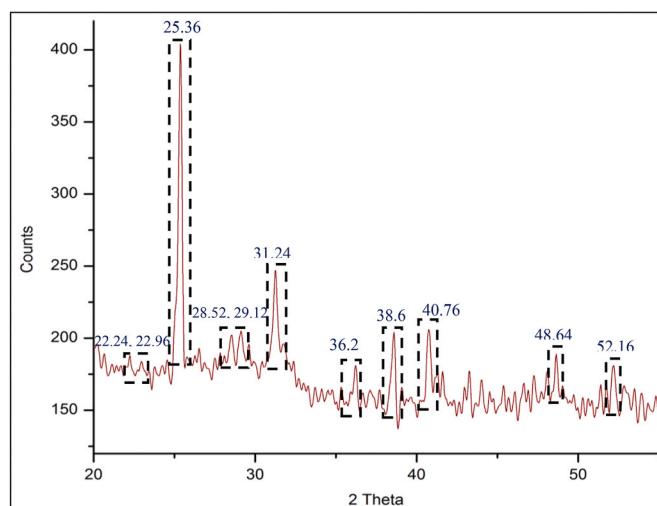


Fig. 6. XRD pattern in WLP residue.

belongs to thorium phosphate compound ($\text{Th}(\text{PO}_3)_4$). EDS analysis shows that phosphate species in WLP residue not only contain pyrophosphate (P_2O_7)⁴⁻ and orthophosphate (PO_4)³⁻ as shown in FTIR analysis but also polyphosphate species (PO_3)¹⁻ in WLP. Thus from SEM/EDS and FTIR analysis, we can make an early assumption that thorium in

Table 3
Thorium compound detected in WLP by XRD analysis.

Element	JSPD No.	XRD Peak WLP (2 θ)
Thorium polyphosphate Th(PO ₃) ₄	PDF-00-025-0968	22.96, 25.36, 31.24
Thorium orthophosphate Th ₃ (PO ₄) ₄	PDF-00-051-1639	22.24, 29.12, 38.6, 48.64
Thorium pyrophosphate ThP ₂ O ₇	PDF-00-016-0230	28.52, 36.2, 40.76, 52.16

WLP residue may not consist of high purity of thorium pyrophosphate.

3.2.3. XRD analysis

XRD analysis test on WLP residue was done to confirm the presence of thorium pyrophosphate (ThP₂O₇) and also to determine the purity of thorium pyrophosphate in the WLP residue. The XRD spectra were analysed by search and match with the JSPD database from Diffrac.Eva software. Fig. 6 shows the XRD pattern in WLP residue. The highlight of this spectrum matched the JSPD database as shown in Table 3, where there are Th(PO₃)₄, Th₃(PO₄)₄ and ThP₂O₇ detected at angle 2 θ between 20° to 60°. In agreement with SEM/EDS and FTIR analysis, the XRD analysis of WLP samples verified that thorium exists in several phosphate compounds instead of solely thorium pyrophosphate (ThP₂O₇) compound. The previous study (Demol et al., 2018), ThP₂O₇ compounds are formed when monazite concentrate is digested with sulphuric acid between 300 °C to 400 °C, whereas the formation of thorium polyphosphate (Th(PO₃)₄) will occurred at the higher temperature between 400 °C to 500 °C. The monazite concentrate processed at Lynas will be heated up to the 650 °C with sulphuric acid during the rare-earth extraction process (Schmidt, 2013). The gradual increases of temperature up to 650 °C may lead to the formation of ThP₂O₇ and Th(PO₃)₄. Aside from that, previous studies (Udayakumar et al., 2020; Palke et al., 2013) also reported the existence of orthophosphate compound (Th₃(PO₄)₄) in the starting monazite concentrate. The formation of (Th₃(PO₄)₄) compound in WLP residue are perhaps related to the partially processed monazite concentrate during the rare-earth extraction process. In addition to that, the re-formation of monazite with a composition closely to the original monazite (starting monazite) was also reported at the temperatures between 650 °C to 800 °C (Demol et al., 2018).

3.2.4. XPS analysis

The wide spectrum in Fig. 7(a) shows the signal of Th, C, O and P atoms displayed in the WLP residue. The phosphate group can be

determined by XPS through two peaks, peak P3/2 and peak P1/2. The binding energy difference between these 2 peaks must be in the range of 0.84 eV. Peak P3/2 for orthophosphate (PO₄)³⁻ group can be detected between 133.0 and 134.0 eV (Siow et al., 2018; Baradarana et al., 2018), while for pyrophosphate group (P₂O₇)⁴⁻ P3/2 can be detected at 132.0–133 eV (Gui et al., 2016; Puziy et al., 2008).

The valence state of phosphorus in WLP residue was studied using X-ray photoelectron spectroscopy (XPS), and the P 2p spectrum and the fitting data are shown in Fig. 7(b) and Table 4. The XPS spectrum was fitted with two components for orthophosphate (PO₄)³⁻ and pyrophosphate (P₂O₇)⁴⁻, for which the P 2p3/2 bond energies (BEs) are 133.85 and 132.85 eV, respectively. XPS analysis proved that both the (PO₄)³⁻

Table 4
XPS fitting results for phosphate compound in WLP residue.

Fitting parameters	Compound types	
	Pyrophosphate (P ₂ O ₇) ⁴⁻	Orthophosphate (PO ₄) ³⁻
BE of P _{3/2} (eV)	132.85	133.85
BE of P _{1/2} (eV)	133.70	134.70
3P peak separation (eV)	0.85	0.85

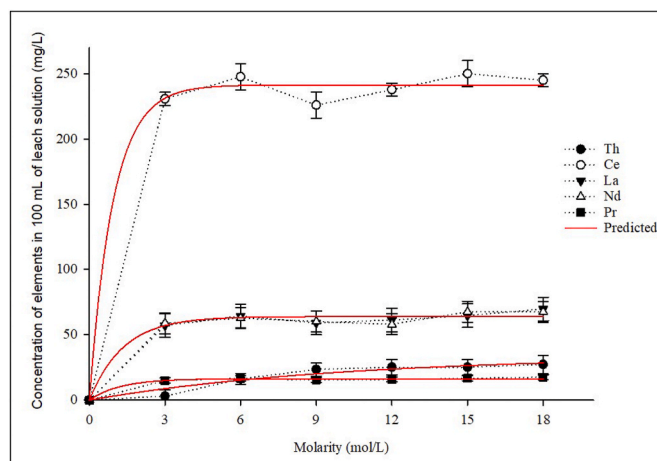


Fig. 8. REE and Th concentration in 100 ml leach solution by (3–18 mol/L) of sulphuric acid digestion process (Baking condition- 2 g of WLP, temperature (200 °C), WLP/acid: 1:5, leaching time is 0.5 h).

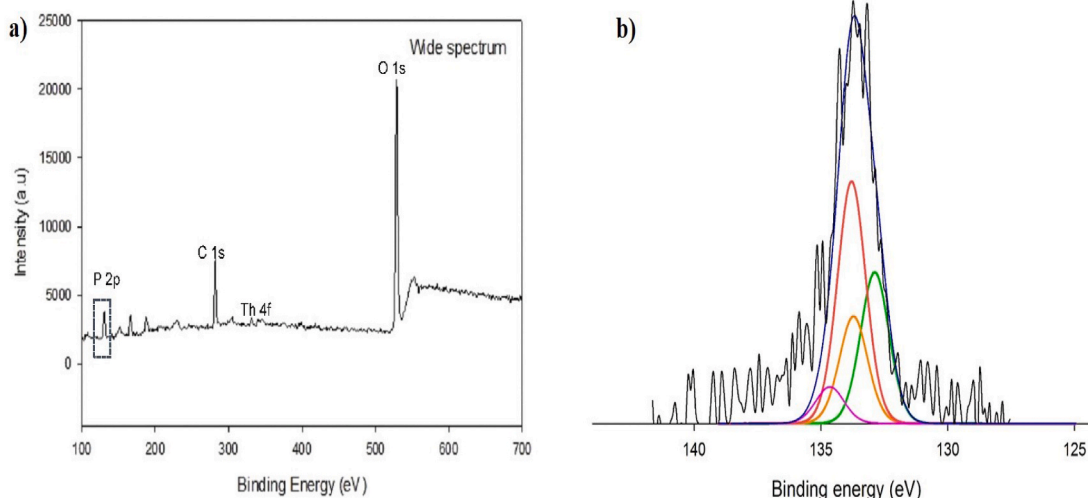


Fig. 7. (a) Wide XPS spectrum of WLP; (b) The fitting peak for phosphate compound in WLP residue.

and $(\text{P}_2\text{O}_7)^{4-}$ valence states are present in WLP residue, consistency with FTIR, SEM-EDS, and XRD analysis before where WLP residue are not highly purity of thorium pyrophosphate.

3.3. Digestion of WLP residue

3.3.1. Molarity of acid effect

Different molarity of sulphuric acid namely, 3 mol/L, 6 mol/L, 9 mol/L, 12 mol/L, 15 mol/L and 18 mol/L (concentrated H_2SO_4) were used in acid bake test. From Fig. 8, the dissolution of thorium increases slowly as the molarity of acid increase and at 18 mol/L of sulphuric acid, the percentage dissolution of thorium is the highest. The finding indicates that thorium inside WLP residue can be dissolved in acid which differs from the previous finding (Al-Areqi et al., 2016; Schmidt, 2013; Yemel'yanov and Yevstyukhin, 1969; Qi, 2018). It must be noted that the previous study reporting on the insolubility of thorium from rare-earth processed residue was not supported by the experimental evidence (Demol et al., 2018). The finding is in agreement with the FTIR, XRD, and XPS analysis performed in this study which indicates the existence of other thorium phosphate compounds in WLP instead of solely ThP_2O_7 . The existence of other thorium phosphate compounds such as thorium orthophosphate ($\text{Th}_3(\text{PO}_4)_4$) either due to the incomplete process of raw material or re-formation of monazite during the rare-earth extraction process (as discussed in 3.2.3) may allow the separation of thorium from WLP residue. It is important to note that it is not possible for thorium in WLP to leach out and into the environment due to the natural process. The leaching process of thorium from WLP for the purpose of separation still requires specific conditions (e.g certain temperature, molarity, and leaching time).

The effect of acid molarity is always associated with pH changes. The pH factor is a crucial parameter due to the formation of metal ion species that differs as the pH changes. The hydroxylation of the species in an aqueous solution also limits the actinide metal solubility which may lead to difference in dissolution potential of thorium in sulphate liquor. As the molarity of acid increases, the pH of the solution becomes more acidic, where at relatively high acidities (below pH 3) more soluble thorium ion species may form (Plinio et al., 2018). Previous thermodynamic data complexation of Th (IV) in sulphate system shows that there are 2 soluble thorium species formed, $\text{Th}(\text{SO}_4)^{2+}$ and $\text{Th}(\text{SO}_4)_3^{2-}$ (Kim and Osseo-Asare, 2012; Organisation for Economic Co-Operation and Development, 2008; Aziman et al., 2019). Therefore, at higher molarity of acid used leads to highest dissolution of thorium due to frequent formation of soluble thorium species in sulphate solution. Besides WLP, industrial residue in China proves that residue from rare earth processing activity can be dissolved in H_2SO_4 acid, giving a 77% dissolution of thorium in leach sulphate solution by using 6 mol/L of H_2SO_4 at 600 °C (Yanliang et al., 2017). Despite success in leaching out thorium from WLP residue up to 50% by using 6 mol/L of H_2SO_4 as shown in Fig. 10, the increasing molarity of H_2SO_4 while using temperatures 3 times lower yields a dissolution of thorium comparable to a previous study (Yanliang et al., 2017).

Besides that, data also shows that molarity up to 3 mol/L of H_2SO_4 provided max loading dissolution of the REE element. An early study on the dissolution of REE elements from other industrial waste or mineral ores in sulphuric acid shows that at 4 mol/L of H_2SO_4 at 60–90 °C, it started becoming constant (Rychkov et al., 2018; Ilgin et al., 2018). Results obtained in this study for the REE element almost similar to the previous outcome. Nevertheless, for element Ce, there is different pattern obtained compared to other REE elements in this study where at molarity 9 mol/L of H_2SO_4 , the dissolution of Ce seems to be decreasing. This may result from the reprecipitation of REEs via calcium sulphate formation (Rychkov et al., 2018; Rina et al., 2015) which is readily formed wherever calcium and sulphate are present together in aqueous solutions (Azimi and Papangelakis, 2010). The presence of calcium in WLP residue is proven by the EDS spectrums shown in Fig. 4(b).

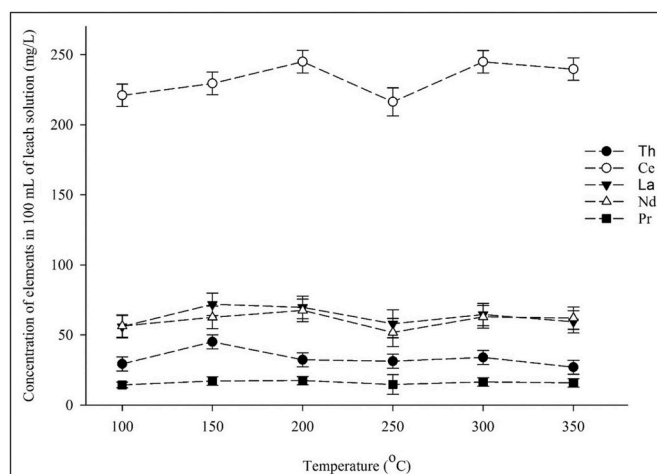


Fig. 9. REE and Th concentration in 100 ml leach solution by concentrated sulphuric acid digestion process (Baking condition- 2 g of WLP, temperature (100–350 °C), WLP/acid: 1:5, leaching time is 1 h).

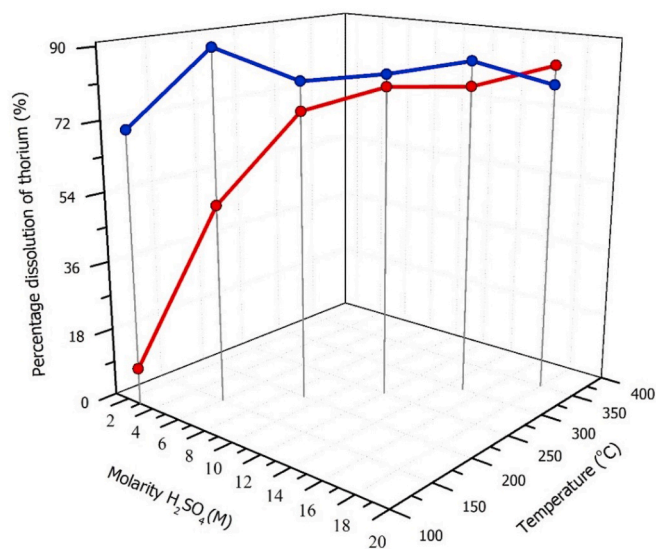


Fig. 10. Percentage of thorium dissolution in WLP affected by different parameters of temperature and molarity of sulphuric acid.

3.3.2. Temperature effect

Effect of temperature on the dissolution of thorium by using concentrated sulphuric acid (H_2SO_4) was run between 100 °C and 350 °C. Since concentrated sulphuric acid (18 mol/L) obtains the highest dissolution of thorium, thus 18 mol/L of H_2SO_4 was used and tested with different temperature effects. From Fig. 9, Ce recorded the highest concentration in the leach solution and followed by other RE elements like La, Nd, and Pr. At temperature 250 °C, the dissolution concentration of the RE element for Ce, La, and Nd seems to be decreasing. These data were consistent with a previous study (Loren et al., 2018), where it was reported that the highest REE dissolution from monazite sulphuric acid digestion was at 210 °C while at 250 °C the dissolution of REE decreases. Recent research shows that 210–220 °C was the best temperature for the dissolution of REE elements in the sulphuric acid medium (Wan Ibrahim et al., 2018; Rabie et al., 2006).

Based on Fig. 9, the dissolution of thorium at 150 °C was highest while at temperature 200 °C the dissolution of thorium started to decrease and keep constant. From the graph, at temperature 300 °C there is an increase dissolution of thorium but the difference between the previous temperatures was just 2–5%. This 2–5% difference does not

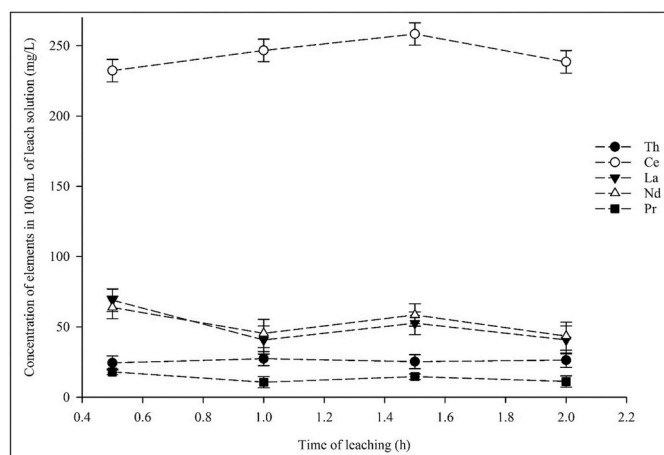


Fig. 11. REE and Th concentration in 100 ml leach solution by concentrated sulphuric acid digestion process (Baking condition- 2 g of WLP, temperature 150 °C, WLP/acid:1:5, leaching time (0.5–2.0 h).

change the value significantly dissolution of thorium at 300 °C. It is shown that at temperature 150 °C, thorium almost completely dissolves using concentrated sulphuric acid. Previous study (Cui et al., 2013) reported that the temperature for acid baked of rare-earth residue from Bayan Obo rare earth concentrated almost near to the temperature obtained from this study. Rare earth residue was baked with sulphuric acid (H₂SO₄) with concentration 1–4 mol/L at boiling point for 1–2 h. The result shows that the recovery of thorium from the rare-earth residue by acid bake is up to 90%. From this data and previous research, it proves that thorium inside rare earth processing residue such as WLP residue can be dissolved at temperature 150 °C.

3.3.3. Leaching time effect

The dissolution performance of thorium from WLP residue also affected by leaching time. Leaching time tested with varies times, from 0.5 to 2 h, together with the same amount of water and room temperature. The effect of reaction time on the leaching rate of the REE element and thorium is shown in Fig. 11. The result shows that the reaction time influences the leaching rate of thorium and the leaching rate starts to become constant at 1 h of leaching time. However, the leaching rate for REE elements shows different patterns, where the leaching rate of La, Nd, and Pr elements over time seems to fluctuate. The differences between the time of leaching are an insignificant effect while for Ce element, the highest leaching rate is at 1.5 h.

A previous study (Guo et al., 2018) reported that the process of sulphuric acid leaching reaction with mineral generates calcium sulphate. The formation of calcium sulphate hinders the leaching reaction. Therefore, extending leaching time by 2 h or more helps the contact reaction between sulphuric acid and the mineral grain surface, which enhances the leaching rate as a result. Consequently, the leaching rate affected by the leaching time for WLP may improve especially for REE elements until a constant leaching rate is obtained. The optimum leaching time thorium for WLP residue in this study is at 1 h.

4. Footnotes on recovery of thorium from rare-earth processed residue

Thorium (Th) usually exist in the form of phosphate compound along with rare-earth (REE) elements [(REE, Th)PO₄]. The separation, extraction, and purification process of rare-earth elements from ores will produce residue with high concentrations of thorium. The increasing demand for rare-earth elements in the application of advanced technology has increased the mining and extraction activity around the world. The main reasons why thorium in post-processed rare-earth

residue should be recovered are;

4.1. Impact on environment and society

The residue generated by the rare-earth processing industry will either be stored inside the facilities without any further treatment or disposed of in a land-based disposal facility. As the quantity of the radioactive residue increases over the years, this situation develops a negative perception and raises concern among the public especially relating to both environmental and radiological impact issues. For example, the Chinese government reported being struggling with the toxic waste that has caused significant damage to the environment due to the rare-earth extraction activities (Michael, 2019).

The rare-earth extraction activities by Lynas Advanced Materials Plant (LAMP) in Malaysia also led to social and environmental conflict amongst the public (Saleem, 2014). The radioactive contamination that happened 20-years ago in Bukit Merah, Perak as a result of rare-earth processing activities that belonged to the Asian Rare-Earth (ARE) caused negative perception among the public that leads to activism against this sector (Aziman and Ismail, 2020). Even though the presence of the RE refinery LAMP in Malaysia is in line with the government's efforts to turn the country into a regional manufacturing hub of energy-efficient vehicles (EEV) but the development of LAMP faced heavy resistance such as public protest and political interferences. It is worth noting that public acceptance is consequential for rare-earth processing technology which will help in the endorsement of the governmental policies in elevating Malaysia's automotive industry to an EEV hub of Southeast Asia (National Automotive Policy NAP, 2014).

Though the country's economy benefits from the industry, the local community cannot be denied: any significant decrease in public acceptance of rare-earth processing technology could jeopardize the government policies. Thus there is a clear need to find the best solution to treat the radioactive residue as further development of the RE industry in Malaysia should proceed parallel with public communication.

Therefore, the idea of reused and recycle the post-processing rare-earth residue is believed to help to gain public acceptance towards the RE industry in Malaysia. By recycling and reusing the residue as a source of recovering thorium, the expected volume of the waste that will be generated should reduce. Aside from that, the public concern towards radiation could also be minimized as the radiological risk towards the public is reduced due to the reduction of thorium content in the residue from the separation phase if complete segregation could be achieved. Thus, recovery of thorium from residue is capable of reducing the volume of waste and minimizing radiological risk which are promising factors that could improve public acceptance in the RE industry. Recovery of thorium could give positive sentiments while increasing positive perceptions towards the RE industry in Malaysia. Good feedback or sentiments, positive perception, and risk perception will lead to better public acceptance and ultimately open up more development of the RE industry in Malaysia as this is in line with government policies.

4.2. Sustainable resources of thorium

Thorium is known as an interesting resource for the application as nuclear fuel since the beginning of the nuclear era. Thorium has several advantages compared to the uranium fuel: it is sustainable, reduces radiotoxicity, and proliferation risk (IAEA, 2005). In addition to that, the conventional uranium resources are expected to last for about 80 years based on the current uranium consumption (Ismail and Yim, 2015). Comparatively, thorium is a promising candidate to be utilized as an alternative nuclear fuel to replace uranium (Lainetti, 2015). The study on thorium recovery from rare earth processed residue helps in the reusability and recyclability of the residue to meet energy demand in the next future.

The total number of thorium resources in the world is estimated to be around 6 205 300–6 212 300 tonnes (IAEA, 2019). These thorium

Table 5
Estimated tonnes thorium can be recovery from by-product around the world.

Activities/Owner	Country/Status	Capacity (tonnes/year)
Richards Bay/RBM, Rio Tinto	S. Africa/operating	1683
Murray Basin/Iluka	Australia/operating	859
Eucla Basin/Iluka	Australia/operating	509
Perth Basin/Iluka	Australia/operating	177
Concord, Virginia/Iluka	USA/operating	93
Orissa/India Rare Earths	India/operating	240
Steenkampskraal/Great Western	S. Africa/in planning	1176
Bokan Mountain/Ucore	USA/in planning	29
Mountain Pass/Molycorp	USA/operating	67
Bear Lodge/Rare Element Res.	USA/in planning	134
Mt. Weld Australia/Lynas	Australia/operating	94–106
Araxá MBAC	Brazil/in planning	373
Total estimated		5434

Sources for capacity: by-product: see [Jordan and Eggert \(2014\)](#) and [Jordan et al. \(2015\)](#).

resources are being classified into five types of deposit: carbonatite, placer (heavy mineral sand), vein, alkaline, and “other” ([NEA and IAEA, 2012](#)) which thorium can be obtained through mining activities. However, increasing mining activities in order to obtained thorium will be lead to new and more complicated social and environmental issues.

Thorium also could be obtained from industrial by-product such as from rare-earth mining and processing activities. Thus, rather than open up a new mining area for thorium extraction and processing, the industrial by-products that contains a high concentration of thorium should be treasured as thorium sources as it will reduce the social and environmental related issues. The expected thorium yield that could be extracted from by-products worldwide is given in [Table 5](#). From the table, it can be concluded that in one year of operating rare-earth mining activities, there are about 5434 tonnes of additional thorium per year and this number will keep increasing until processing plants stop their operation ([Jordan et al., 2015](#)).

Lynas, Malaysia contributed an additional 2% of thorium per year from by-product residue around the world. In the context of Malaysia, about 2636 tonnes of Malaysian monazite was produced over a period of 5 years (2006–2010) and it could be estimated that Malaysian monazite contains about 184.5 tonnes of thorium. By comparing to the Malaysian monazite, within 5 years of operation of rare-earth plant processing, Lynas can produce about 530 tonnes of thorium compared to the monazite. Thus the volume of residue generated from the rare-earth industry will be significantly reduced as thorium could be recovered from it compared to opening up new thorium mining plants. Therefore, it is paramount to see that rare-earth processed residue is the new frontier in sustainable thorium resources for the world in the future.

5. Conclusion

The research finding provides scientific evidence that thorium in WLP exists in other thorium phosphate compounds ($\text{Th}(\text{PO}_3)_4$) and ($\text{Th}_3(\text{PO}_4)_4$) and not solely as thorium pyrophosphate (ThP_2O_7) as previously assumed. The finding also indicates that thorium in WLP can be separated into a thorium leach solution that can further investigated for the recovery process. It is important to clarify that thorium in WLP only can be leach and recovered through a specific digestion process which is not possible to occur in the natural environment. The reuse and recycling of WLP residue for thorium recovery may not only solve the environmental issue regarding the disposal huge amount of radioactive waste, but it also provides sustainable thorium resources as a long-term energy security. The recovery of thorium from WLP also minimizes the volume of radioactive waste as well as the radiological concerns associated with the waste that may lead to better acceptance among the public towards the rare-earth industry. In conclusion, the possibility of separating thorium from rare-earth processed residue may open up a promising future on utilizing the residue for the benefit of other

applications, especially in the nuclear industry that finally may turn waste into wealth.

Credit author statement

Eli Syafiqah Aziman: Experimental, Formal analysis, Writing - original draft. **Aznan Fazli Ismail:** Investigation, Experimental, Formal analysis, Writing - original draft, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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