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Original Article

Structural and morphological characterization of Thai monazite ore processing samples♣

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Abstract

Monazite ore is mainly composed of rare earth elements (such as Ce, Nd, La, etc.). These rare earth elements are widely used in several high technology and industrial products. Thailand Institute of Nuclear Technology has performed research on the separation and purification of rare earth elements from Thai monazite ore for supporting industrial applications. In this work, the raw material, intermediate and by-product samples obtained from Thai monazite ore processing were characterized by various physicochemical techniques (WDXRF, XRD and SEM-EDS) for understanding their structural and morphological characteristics. The WDXRF analysis showed that the monazite ore sample contained primarily cerium (30.37 wt% of CeO_2) which matched well with the XRD result. An increase in CeO_2 concentration up to 39.19 wt% and 64.62 wt% in the intermediate mixed rare earth and cerium hydroxide cake samples were observed after alkali digestion and nitric acid leaching of monazite ore, respectively. No rare earth elements could be detected in the tri-sodium phosphate by-product. Thorium oxide at 6.34% in uranium cake sample was observed. A considerable amount of NaOH in thorium cake sample was noticed.

Keywords: monazite ore processing, structural, morphological, characterization, rare earth element

1. Introduction

In Thailand, monazite ore is mainly associated with tin deposits, which were mined in several provinces, although the majority of tin production were from Phuket and Phang-nga provinces (Injarean, Nuchdang, Leelanupat, & Rattanaphra, 2018). Monazite is a good source of a number of rare earth elements (REEs), especially cerium (Ce), lanthanum (La), and neodymium (Nd), which can be used in several industries. Monazite also contains some thorium needed for making high quality camera lenses and certain scientific equipment. Thailand Institute of Nuclear Technology has conducted research on the decomposition of monazite ore using alkali method. The major steps of the process include: (1) the digestion of monazite ore with diluted alkali, (2) the crystallization of tri-sodium phosphate by-product, (3) the removal of radioactive materials (uranium U and Thorium Th), (4) the extraction of REEs, and (5) the purification of individual REEs using ion exchange. The intermediate, by-product and product samples in each step of the process need to be evaluated for quantities of U and Th in order to limit and control the levels of radioactive materials in those samples. In

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addition, the elemental compositions and structural properties of the samples also need to be evaluated for improvement of REEs product quality and process efficiency.

There have been three main methods for the extraction of REEs from monazite ore namely sulphuric acid decomposition (acid bake), decomposition with sodium/potassium hydroxide (alkali pug bake), and high-temperature roasting with calcium carbonate or sodium carbonate (Berry, Agarwal, Galvin, & Safarzadeh, 2018). Berry, Agarwal, Galvin, and Safarzadeh (2018) investigated the use of sulphuric acid to bake monazite concentrate for the leaching of REEs. It was found that at the optimum conditions having mass ratio of sulphuric acid to monazite concentrate of 1:1, baking temperature of 250 °C for 4 h, this could leach out REEs by 65% while 2-5% of uranium and thorium were extracted as well. They also suggested that the acid bake used in their study consumed more reagent and produced phosphoric acid, which had no appreciable commercial value. Meanwhile, alkali pug bake process done previously showed to be less reagent consuming and produced sodium phosphate as by-product, which can be utilized as a fertilizer (Berry, Galvin, Agarwal, & Safarzadeh, 2017). Kumari *et al.* (2015) studied the thermal decomposition of Korean monazite using Na_2CO_3 and NaOH roasting processes to recover REEs. The results showed that complete conversion of rare earth phosphate into its oxides was obtained when the monazite was roasted with Na_2CO_3 and NaOH at 900 and 400 °C, respectively for 120 min and using the ratio of monazite to alkali of 1:1. The REEs recovery of >90% could be achieved after the roasted samples were leached with 6M HCl for 2 h at 80 °C. Samin, Setiawan, Anggraini, and Sunanti (2020) carried out the decomposition of monazite sand with NaOH at 140 °C following the dissolution with HCl at 80 °C, then the separation of rare earth from uranium and thorium could be done using NaOH. The obtained rare earth hydroxide was characterized by XRF and XRD techniques. The results demonstrated that the rare earth hydroxide formed perovskite compound ($La_{0.9}Sr_{0.1}CrO_3$), NaF, etc. The main rare earth components were found to be Ce (27.67%), La (13.85%) and Nd (8.45%).

Meanwhile, Huang *et al.* (2019) studied the decomposition of mixed rare earth concentrate (bastnaesite, monazite and fluorite) with NaOH using microwave heating. The reaction temperature was 450 °C, microwave heating time was 40 min, and NaOH content was 45% in the study. It was found that the final products of this process consisted of $Ce_{0.5}Nd_{0.5}O_{1.75}$, $Ca_{10}(PO_4)_6(OH)_2$ and NaF. Some particles of the sample product appeared to be a loose with porous structure surface morphology while other particles were covered with rod-shaped crystals on their surfaces. Udayakumar *et al.* (2018) investigated the characterization and elemental analysis of uranium, thorium and rare earth elements in Malaysian monazite concentrate using various non-destructive techniques; XRF, XRD and SEM-EDX. The U and Th levels of 0.25 and 8.52 wt%, respectively, were detected by XRF. The results from SEM showed that the monazite had irregular shapes and sizes. In addition, U and Th can be observed as trace and major elements in the mineral, respectively, by EDX. The XRD confirmed that the main mineral phases of monazite included $LaPO_4$, $CePO_4$ and $NdPO_4$. However, stronger X-ray reflection from the rare earth phosphates caused the disappearance of $Th_4(PO_4)_4$ phase. Yanhui *et al.* (2012) examined the decomposition of bastnasite and monazite rare earth concentrates by alkali solution using a rotary electric furnace. The results showed that the decomposition ratio of rare earth concentrates and the oxidation ratio of cerium could exceed 93% at calcination temperature above 300 °C. The XRD results revealed that the obtained alkali cake was mainly composed of Ce_7O_{12} and $Ce_{0.75}Nd_{0.25}O_{1.875}$ phases and had no peaks of rare earth hydroxide. Na_2CeO_3 and $NaREO_2$ can be also observed in the XRD patterns.

In this study, samples from each step in monazite ore treatment were characterized for chemical composition, and structural and surface morphology by using WDXRF, XRD and SEM-EDS techniques. Data obtained from this study will be used to design method(s) for controlling and improving the efficiency of the treatment process and also to limit as well as regulate the levels of uranium and thorium radioactive materials.

2. Materials and Methods

2.1 Monazite concentrate processing

Thailand Institute of Nuclear Technology has carried out the Thai monazite ore processing in order to extract and purify rare earth elements for industrial applications. Thai monazite ore processing involves breaking down monazite ore by alkali method. In this step, the monazite ore was treated with 50 wt% NaOH at about 140 °C for 3-4 h. The alkali treatment of monazite ore is shown by Equation (1)

$$REE(PO_4) + 3NaOH \rightarrow REE(OH)_3 + Na_3PO_4 \qquad (1)$$

The product obtained from this step is intermediate mixed rare earth with tri-sodium phosphate as by-product. The intermediate mixed rare earths, containing rare earths, uranium and thorium, were dissolved with HCl and then precipitated in the form of hydroxides using 20 wt% NaOH at pH 4.5. The hydroxide cake, mainly containing uranium and thorium, was then dissolved with diluted HNO_3. The uranium was separated from thorium by solvent extraction with 5% v/v tributyl phosphate (TBP) in kerosene. The organic phase containing the uranium was scrubbed and stripped with HNO_3 and water, respectively. The yellow cake ($(NH_2)_2U_2O_7$) was obtained by the precipitation of aqueous phase with NH_4OH. For getting a $Th(OH)_4$ cake, the solution from uranium extraction was extracted with 40% v/v TBP in kerosene.

The mixed rare earths chloride solution ($RECl_3$) from the precipitation of uranium and thorium was precipitated with 20 wt% NaOH and cerium was leached with HNO_3 to obtain cerium hydroxide cake. The rare earth elements were extracted with 50% v/v TBP and then purified using ion exchange technique to archive high purity individual rare earths.

2.2 Sample preparation

All samples were obtained from Thai monazite ore processing at Thailand Institute of Nuclear Technology (Public Organization). The samples were ground and sieved to the size range of 45 μm < d < 300 μm. The fine samples were then dried to constant weight at 110 °C for 12 h.

2.3 Wavelength dispersive X-ray fluorescence (WDXRF) analysis

Quantitative analysis of elements in all samples was carried out by using a Bruker S8 Tiger wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. A sample mass of 0.82 g was mixed with a flux agent. The flux agent was the mixture of lithium tetraborate and lithium (4:1) (by weight). Ammonium iodide amount of 0.08 g was added as releasing agent. The total weight of the mixture was 6.9 g. Then, the prepared sample was dissolved in a platinum crucible at 1000 °C for 2 min in a fusion machine.

2.4 X-ray powder diffraction (XRD) analysis

XRD analysis was used for phase identification and crystal structure determination of the samples. All samples were analyzed using a Bruker-AXS, D8 AVANCE equipped with Cu Kα radiation (λ = 1.5406 Å) operating at 30 kV and 30 mA. The measurements were performed in the 2θ angle range of 20-90° with a 2θ step size of 0.039° and a step time of 1 sec.

2.5 Scanning electron microscopy/energy dispersive X-ray spectrometer (SEM-EDS) analysis

The samples were analyzed for their morphological and chemical compositions with Tescan Vega 3 scanning electron microscope (SEM) equipped with an Oxford X-Max Silicon Drift Detector energy dispersive X-ray spectrometer (EDS) using an acceleration voltage of 20 kV. SEM images were captured via retractable solid state back scattered electron detector and the EDS mapping mode was used for elemental analysis.

3. Results and Discussion

3.1 Elemental analysis by WDXRF

Chemical compositions of different Thai monazite ore processing samples determined by WDXRF analysis are shown in Table 1. The monazite ore sample was found to be a monazite concentrate with total rare earth oxides at 58.54%. The presence of P_2O_5 (21.69%) confirmed that the monazite ore was composed of rare earth phosphate minerals. Cerium (CeO_2 = 30.37%) was found predominantly over the other light rare earths (LREES) La (La_2O_3= 10.84%), Nd (Nd_2O_3 = 10.67%), Pr (Pr_6O_{11} = 2.13%) Gd (Gd_2O_3 = 1.11%). Some of heavy rare earths (HREES) such as Y (Y_2O_3 = 2.78%), Dy (Dy_2O_3 0.50%) and Er (Er_2O_3 =0.14%) were also observed. The radioactive elements, such as uranium and thorium, are also associated with rare earth elements at 0.47 and 8.64 %, respectively. The elements Fe, Si, Nb, Ti, Ca, Al and Ta could be detected as well. The chemical compositions of monazite ore from nearby countries are summarized in Table 2. According to Table 2, monazite from Thailand, Malaysia and Myanmar have similar chemical compositions and rare earth contents. Meanwhile, monazite from Bangka Island, Indonesia, showed a lower rare earth contents than those areas. The intermediate mixed rare earth and tri-sodium phosphate was obtained from alkali digestion of monazite ore (Equation 1). It can be seen that the concentrations of almost all elements in intermediated mixed rare earth sample were increased except for P_2O_5. A considerable amount of Na_2O can be noticed, introduced by excessive NaOH use in the digestion step. For tri-sodium phosphate (Na_3PO_4), no any elements could be identified by WDXRF, except for Na_2O and P_2O_5.

Table 1. Chemical compositions of different Thai monazite ore processing samples by wt% as measured by WDXRF

Sample		Concentration (wt%)																		
		CeO_2	P_2O_5	La_2O_3	Nd_2O_3	ThO_2	Fe_2O_3	Y_2O_3	SiO_2	Na_2O	Nb_2O_5	Pr_6O_{11}	Gd_2O_3	TiO_2	CaO	Dy_2O_3	UO_2	Al_2O_3	Ta_2O_5	Er_2O_3
Monazite ore	Mean (wt%)	30.37	21.69	10.84	10.67	8.64	4.20	2.78	2.42	nd	1.33	2.13	1.11	0.76	0.71	0.50	0.47	0.51	0.32	0.14
	SD	0.50	0.71	0.21	0.07	0.05	0.06	0.02	0.02	-	0.04	0.11	0.06	0.01	0.01	0.02	0.01	0.01	0.03	0.00
	CV	1.63	3.25	1.90	0.63	0.62	1.35	0.77	0.70	-	2.75	5.01	5.37	1.93	0.71	3.95	1.62	1.20	7.76	3.69
Intermediate mixed rare earth	Mean (wt%)	39.19	3.77	13.94	13.75	9.62	1.48	2.77	1.68	4.36	0.75	2.47	1.29	1.03	0.73	0.46	0.44	0.56	0.67	0.14
	SD	0.25	0.37	0.40	0.31	0.23	0.03	0.07	0.04	0.26	0.02	0.13	0.01	0.07	0.05	0.01	0.02	0.00	0.03	0.00
	CV	0.63	9.91	2.89	2.27	2.39	2.28	2.38	2.11	5.87	2.69	5.37	0.77	6.65	6.27	1.73	3.59	0.87	4.40	0.83
Tri-sodium phosphate	Mean (wt%)	nd	36.33	nd	nd	nd	nd	nd	nd	64.63	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
	SD	-	0.68	-	-	-	-	-	-	1.92	-	-	-	-	-	-	-	-	-	-
	CV	-	1.87	-	-	-	-	-	-	2.97	-	-	-	-	-	-	-	-	-	-
Cerium hydroxide cake	Mean (wt%)	64.62	nd	5.58	14.33	nd	nd	3.51	nd	nd	2.22	2.89	1.85	nd	0.20	0.83	nd	nd	nd	0.15
	SD	0.55	-	0.01	0.50	-	-	0.10	-	-	0.06	0.09	0.06	-	0.01	0.02	-	-	-	0.01
	CV	0.85	-	0.24	3.34	-	-	2.97	-	-	2.51	3.13	3.22	-	3.36	2.77	-	-	-	4.88
Uranium cake	Mean (wt%)	nd	nd	nd	nd	6.34	nd	nd	0.19	0.59	nd	nd	nd	nd	nd	nd	87.56	nd	nd	nd
	SD	-	-	-	-	0.07	-	-	0.00	0.02	-	-	-	-	-	-	0.10	-	-	-
	CV	-	-	-	-	1.13	-	-	1.90	2.76	-	-	-	-	-	-	0.12	-	-	-
Thorium cake	Mean (wt%)	nd	nd	nd	nd	85.99	0.13	nd	nd	12.79	nd	nd	nd	nd	0.20	nd	0.57	nd	nd	nd
	SD	-	-	-	-	0.73	0.01	-	-	0.14	-	-	-	-	0.01	-	0.01	-	-	-
	CV	-	-	-	-	0.85	3.97	-	-	1.08	-	-	-	-	7.03	-	2.17	-	-	-

nd = not detect

Table 2. Chemical compositions of monazite from different areas

Element	Concentration (wt%)			
	Thailand[a]	Mongmit Myitsone, Myanmar[b]	Malaysia[c]	Bangka Island, Indonesia[d]
CeO_2	30.37	27.21	30.19	12.15
La_2O_3	10.84	10.73	14.68	4.98
Nd_2O_3	10.67	8.90	9.52	4.95
Y_2O_3	2.78	0.89	2.46	4.05
$Pr_{11}O_6$	2.13	1.77	2.09	1.14
Sm_2O_3	-	1.02	2.11	0.72
Gd_2O_3	1.11	0.66	2.12	0.59
Dy_2O_3	0.50	0.20	0.55	0.75
Er_2O_3	0.14	-	0.10	0.46
P_2O_5	21.69	19.34	18.06	20.19
Fe_2O_3	4.20	1.25	0.82	-
SiO_2	2.42	4.26	-	-
Nb_2O_5	1.33	-	-	-
TiO_2	0.76	3.54	0.62	-
CaO	0.71	-	0.54	-
Al_2O_3	0.51	-	-	-
ZrO_2	-	0.56	1.78	-
Ta_2O_5	0.32	-	-	-
ThO_2	8.64	8.16	7.16	2.80
UO_2	0.47	0.39	2.07	0.14

[a]This study, [b]Tar, Myo, Hlaing and Win (2017), [c]Jaffary *et al.* (2019), [d]Purwanti *et al.* (2020)

In the next step, the selective precipitations of uranium, thorium and rare earths were carried out via the HCl dissolution of intermediate mixed rare earth followed by NaOH precipitation. The obtained mixed rare earth chloride solution was precipitated with NaOH and subsequently leached with HNO_3 to form cerium hydroxide cake. It was found that this process could greatly enrich the Ce content from 39.19 to 64.62%. A slight increase in content of REEs; Nd (from 13.75 to 14.33%), Y (from 2.77 to 3.51%), Pr (from 2.47 to 2.89%), Gd (from 1.29 to1.85%), Dy (from 0.46 to 0.83%) and Er (from 0.14 to 0.15%), was also observed. Meanwhile, La content decreased from 13.94 to 5.58%. Normally, the optimum pH for La precipitation is greater than 7, while pH in the range 6-7 is favorable for precipitation of Ce, Nd, Y, Pr, Gd, Dy and Er. A small amount of some elements, such as Nb and Ca, still remained in the sample. There were no uranium and thorium present in the sample, indicating a quite high separation efficiency. The cake containing uranium and thorium obtained from the HCl dissolution step was dissolved with HNO_3. Subsequently, uranium was separated from thorium by solvent extraction with TBP. The WDXRF analysis of uranium cake sample revealed that the extraction process could reach uranium content up to 87.56%, but it was found to be contaminated with thorium (6.34%), Si (0.19%) and Na (0.59%). For thorium cake sample, the thorium content of 85.99% could be observed with small concentrations of U, Fe and Ca. There was a large amount of Na (12.79%) remaining in the sample.

3.2 Phase and crystal structure identification by XRD

Figure 1 shows the XRD patterns of samples from different stages of Thai monazite ore processing, and their unit cell parameter, unit cell volume, XRD-density, average crystallite size and crystal structure are gathered in Table 3. The XRD pattern of monazite ore sample indicated that the sample consisted of monazite-cerium, $Ce(PO_4)$ with monoclinic crystal structure. The main reflection peaks at $2\theta = 25.37$, 26.96, 28.79, 29.87, 41.14 and 42.02 were observed which matched well with JCPDS file no. 01-083-0650. This result corresponded well with those mentioned by Udayakumar *et al.* (2018) and Tar, Myo, Hlaing, and Win (2017). Furthermore, the results were in good agreement with the WDXRF results which indicated high content of Ce and P in the monazite ore sample. This monazite type generally occurs through wet chemistry solid state route (Clavier, Podor, & Dacheux, 2011). The lattice parameters and unit cell volume also agreed well with those reported by Konings, Walter, and Popa (2008). For the intermediate mixed rare earth sample, the diffraction pattern was consistent with cerium neodymium oxide compound ($Ce_{0.5}Nd_{0.5}O_{1.75}$) (Figure 1(b)). Four broad diffraction peaks were observed at $2\theta = 28.17$, 32.43, 46.58, 56.04, representing the (222), (400), (440), (622) crystal planes. The crystal planes were in good accordance with a cubic crystal structure (JCPDS file no. 00-028-0267). The average crystallite size of intermediate mixed rare earth sample was found to be 6.77 nm. Compared with the XRD pattern of monazite ore, it was found that the characteristic peaks of monazite disappeared, indicating the monazite was decomposed into mixed rare earth hydroxide by NaOH.

Meanwhile, the XRD pattern of the cerium hydroxide cake showed a shift of 2θ angles in comparison with the intermediate mixed rare earth (JCPDS file no. 00-028-0266), see Figure 1(b) and 1(d). In addition, the lattice parameter of cerium hydroxide cake sample was found to be 0.5458 nm which is smaller than that of the intermediate mixed rare earth (1.0990 nm). The peak shift and the change in lattice parameter of cerium hydroxide cake indicate that

Table 3. Unit cell parameter, unit cell volume, XRD-density, average crystallite size and crystal structure of different Thai monazite ore processing samples

Compound	Lattice parameter (Å)			Unit cell volume (Å^3)	Density (g/cm^3)	Average crystallite size (nm)	Crystal structure
	a	*b*	*c*				
Monazite ore	6.7902	7.0203	6.4674	299.93	5.20	59.33	Monoclinic
Intermediated mixed rare earth	10.9900	10.9900	10.990	1327.37	-	6.77	Cubic
Tri-sodium phosphate	11.9100	11.9100	12.6900	1558.89	1.63	56.18	Hexagonal
Cerium hydroxide cake	5.4580	5.4580	5.4580	162.59	6.99	8.42	Cubic
Uranium cake	-	-	-	-	-	55.76	-
Thorium cake	5.5961	5.5961	5.5961	175.25	10.01	74.56	Cubic

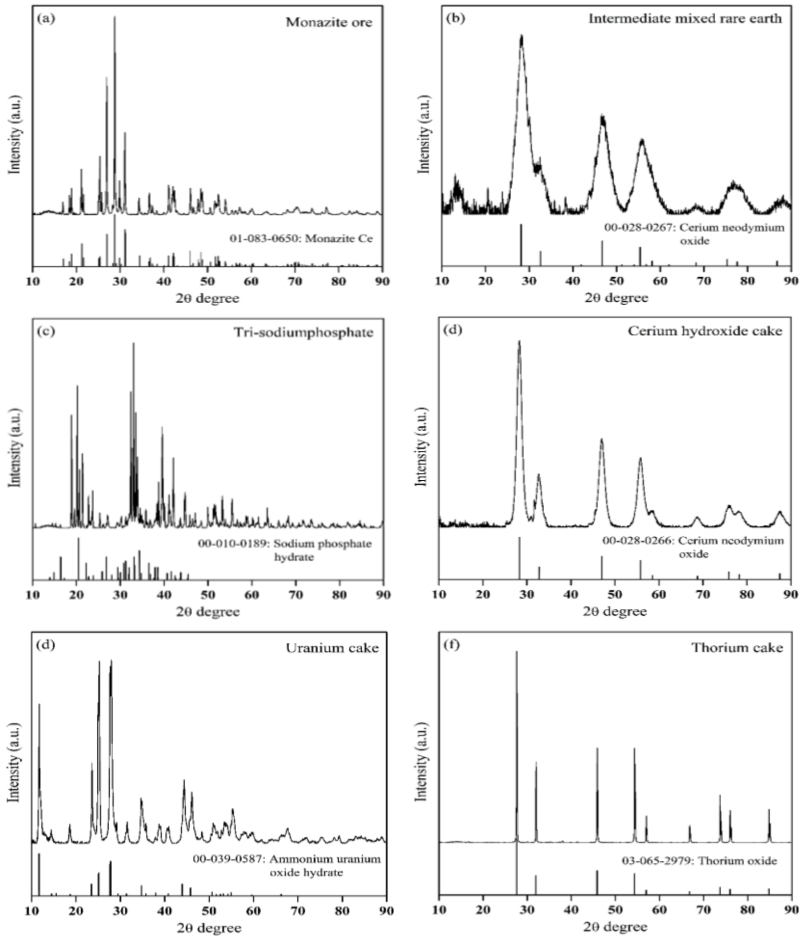

Figure 1. XRD patterns of monazite ore, intermediate mixed rare earth, tri-sodium phosphate, cerium hydroxide cake, uranium cake and thorium cake samples

uranium and thorium can be removed by the precipitation of intermediate mixed rare earth with NaOH at pH 4.5. The shape diffraction peaks appeared at 2θ = 28.29, 32.68, 46.93 and 55.78 and can be indexed to the (111), (200), (220) and (311) planes of face centered cubic phase of pure cerium oxide, indicating the formation of highly pure cerium oxide phase in the sample. All diffraction peaks became shaper and stronger, suggesting improvement in crystallinity of the cerium hydroxide cake sample. Figure 1 (c) shows the XRD pattern of tri-sodium phosphate sample. The major diffraction peaks located at 2θ = 20.20, 26.83, 33.13 and 34.36 can be attributed to the hexagonal phase of sodium phosphate hydrate, $Na_3PO_4.12H_2O$ (JCPDS file no. 00-010-0189). The crystallite size of the sample ranged from 38 to 75 nm. No diffraction peaks associated with rare earths, uranium or thorium can be observed. The characteristic peaks of uranium cake sample situated at 2θ = 24.96, 27.64, 34.65 and 35.79 can be indexed to ammonium uranium oxide hydrate,

$UO_3.NH_3.H_2O$ and matched well the JCPDS file no. 00-039-0587. There were no ThO_2 and Na_2O peaks that could be detected by XRD, even though the WDXRF result as mentioned above showed a significant amount of those compounds in the uranium cake sample. For thorium cake sample, all shape peaks located at 2θ = 27.64, 32.02, 45.86, 54.35, 56.98, 66.84, 73.76, 76.01 and 84.82 corresponding to (111), (200), (220), (311), (222), (400), (331), (420) and (422) planes matched very well with JCPDS file no. 03-065-2979. The diffractogram peaks were indexed to cubic thorium oxide (ThO_2). Although a significant amount of Fe_2O_3, Na_2O, CaO and UO_2 could be identified by WDXRF, those compound peaks were not shown in XRD pattern of the thorium cake sample. The thorium oxide cake sample also exhibited high crystallinity and large average crystallite size (745.57 nm).

3.3 Surface morphology and qualitative elemental composition by SEM-EDS

SEM images and EDS analysis data of the Thai monazite ore processing samples are illustrated in Figure 2-7. The SEM image of monazite grains demonstrates irregular and angular shapes. The major elements detected by the EDS analysis were Ce, Nd, P, La and Th (Figure 2), which is in a good agreement with WDXRF and XRD results. For the intermediate mixed rare earth sampl, see Figure 3, Pr and Sm could be identified by EDS while P was absent, which confirmed the transformation of phosphate compound in monazite ore to Na_3PO_4. As can be seen from Figure 4, the tri-sodium phosphate sample consisted of smooth aggregated particles with particle size ranging within 4-8 µm. The EDS analysis clearly indicated that Na and P elements were the two major components in the tri-sodium phosphate sample. In the case of cerium hydroxide cake (Figure 5), a particle size of around 35 µm was observed. The main elements presented in the sample were Ce, Nd, La, Pr and Sm. Rough surfaced particles of size 30 µm were noted in the uranium cake sample (Figure 6). U element was found to be predominant in this sample. For the thorium cake sample (Figure 7), the SEM image demonstrated agglomerated particles and high content of Th was detected by the EDS analysis.

4. Conclusions

The monazite ore processing consisted of four main stages, namely decomposition of monazite with NaOH at 140 °C, partial dissolution with HCl, uranium and thorium extraction, and selective precipitation of rare earth hydroxide.

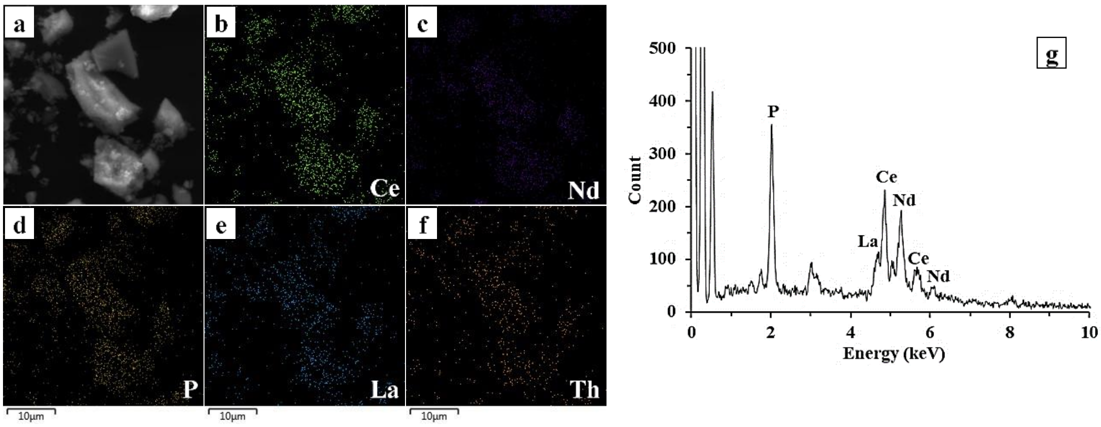

Figure 2. SEM images of monazite ore sample (a), EDS spectra mapping of monazite ore sample: Ce (b), Nd (c), P (d), La (e), Th (f), and EDS spectra of monazite ore sample (g)

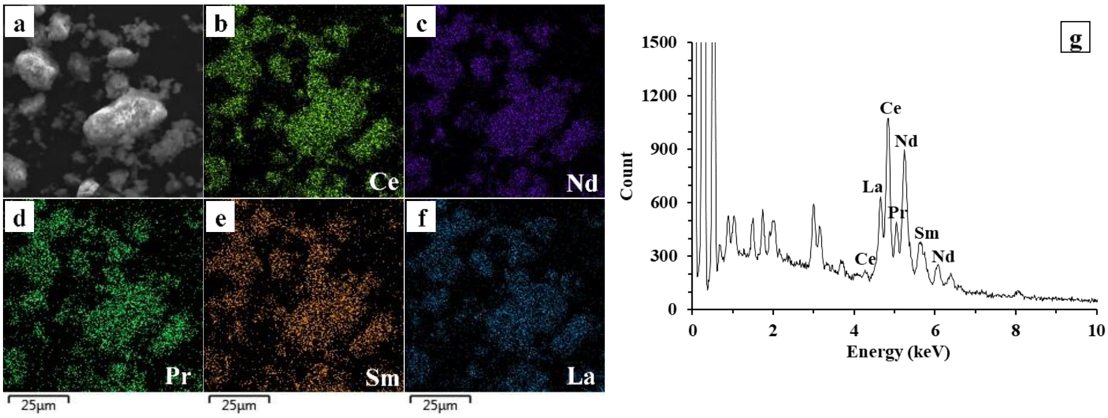

Figure 3. SEM images of intermediate mixed rare earth sample (a), EDS spectra mapping of intermediate mixed rare earth sample: Ce (b), Nd (c), Pr (d) Sm (e), La (f), and EDS spectra of intermediate mixed rare earth sample (g)

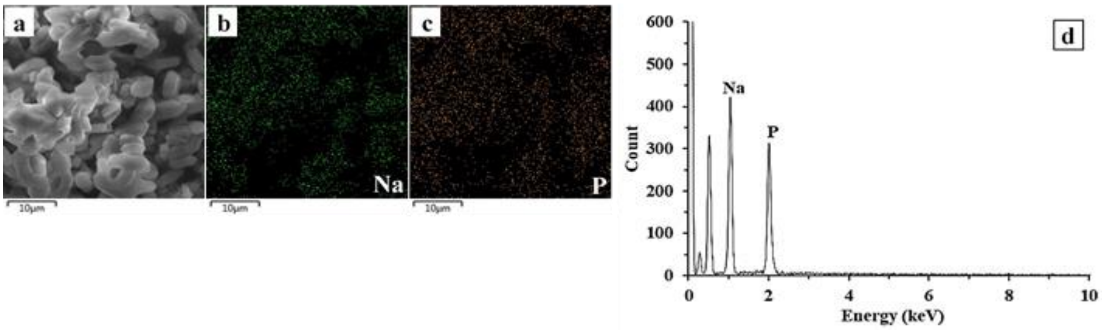

Figure 4. SEM images of tri-sodium phosphate sample (a), EDS spectra mapping of tri-sodium phosphate sample: Na (b), P (c), and EDS spectra of tri-sodium phosphate sample (d)

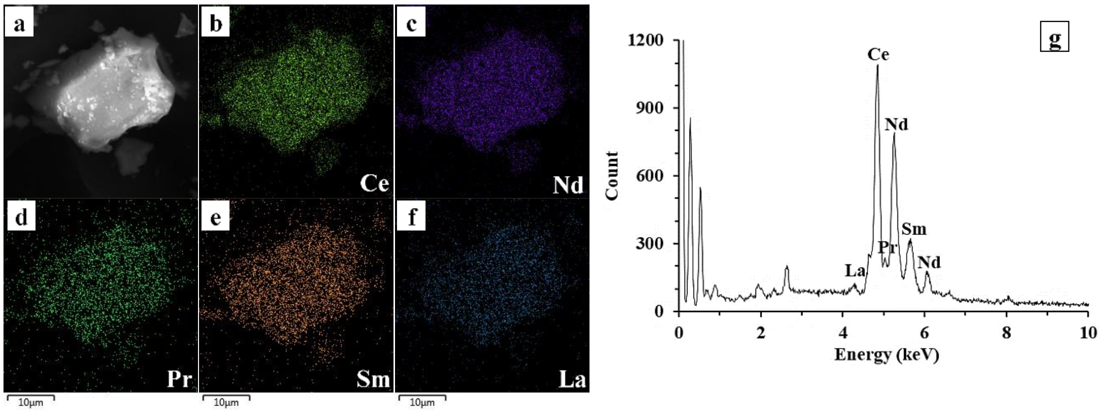

Figure 5. SEM images of cerium hydroxide cake sample (a), EDS spectra mapping of cerium hydroxide cake sample: Ce (b), Nd (c), Pr (d), Sm (e), La (f), and EDS spectra of cerium hydroxide cake sample (g)

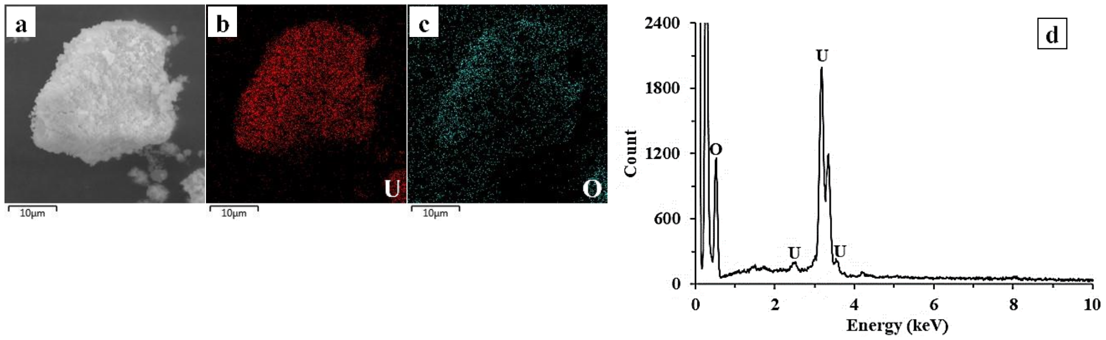

Figure 6. SEM images of uranium cake sample (a), EDS spectra mapping of uranium cake sample: U (b), O (c), and EDS spectra of uranium cake sample (d)

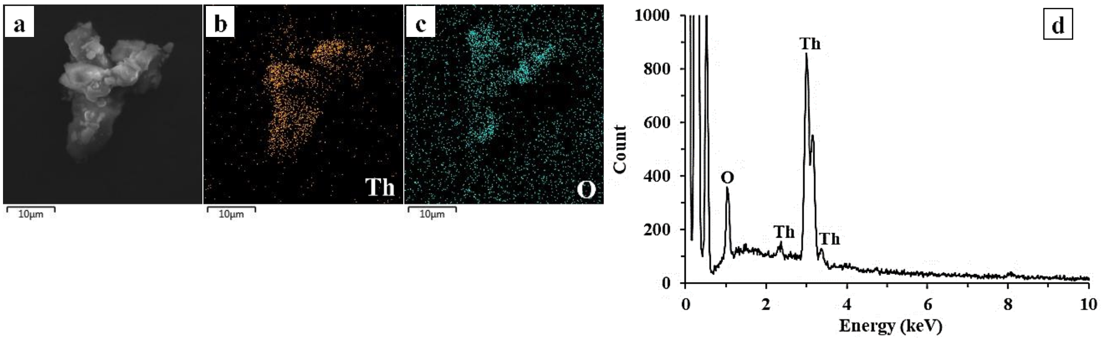

Figure 7. SEM images of thorium cake sample (a), EDS spectra mapping of thorium cake sample: Th (b), O (c), and EDS spectra of thorium cake sample (d)

The characterization of samples from each step of the process was necessary to improve the process performance and control the radioactive material levels. The elemental composition, crystal structure and surface morphology of monazite ore processing samples were characterized by various techniques such as WDXRF, XRD and SEM-EDS. The major phase of monazite ore sample identified by XRD was monazite-cerium and the rare earth elements accounted for almost 60% of the total composition, as detected by WDXRF. After digestion of monazite using NaOH, the intermediated mixed rare earth was obtained and the rare earths content in that sample reached 74%. The dissolution of intermediated mixed rare earth sample with HCl followed by leaching with HNO_3 produced cerium hydroxide cake, and this process could recover 94% of rare earths. The obtained Na_3PO_4 by-product was found to be not contaminated, and can be used as a mineral fertilizer. The presence of significant amount of thorium oxide contamination in uranium cake sample was observed. The thorium cake was contaminated with NaOH. Although the decomposition of monazite ore used in this study is the same as in several studies, we are successful in controlling important operating parameters of the process, such as pH, temperature, and reaction time, which resulted in a high recovery of REEs and high removal efficiency of phosphate. These data will be used to improve the process efficiency and applied to the separation of REEs from other REEs resources. In further studies, the removal of thorium impurity in uranium cake, the elimination of NaOH in thorium cake, and the purification of individual REEs using ion exchange technique will be pursued.

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