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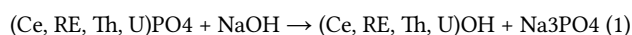
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CHARACTERIZATION OF URANIUM, THORIUM AND RARE EARTHS IN THE DECOMPOSITION PROCESS OF THAI MONAZITE ORE SAMPLES BY X RAY POWDER DIFFRACTION AND WAVELENGTH DISPERSIVE X RAY FLUORESCENCE TECHNIQUES

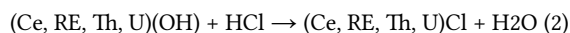
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INTRODUCTION

In Phuket and Phang-nga region of Thailand, monazite ore has been found in association with tin and beach sands deposits. The Thailand Institute of Nuclear Technology has performed the separation and purification of rare earth elements for industrial application. The principal process can be summarized as follows: in the first step, the monazite ore (325 mesh) was digested with 50 wt% NaOH at 140 °C for 3 h the reaction proceeds as:



The obtained hydrous metal oxide cake of Ce, RE, Th and U was dissolved in 35% w/v HCl. The HCl was used to neutralize and reacted with hydroxides to generate chloride compounds solution as follows:



The uranium ($Na_2U_2O_7$) and thorium ($Th(OH)_4$) can be obtained by the selective precipitation of the chloride compounds solution with 20% w/w NaOH at pH 4.5. The solvent extraction using 5%v/v of tributyl phosphate (TBP)/kerosene process was utilized to separate uranium and thorium. The extracted uranium was precipitated with NH_4OH to form yellow cake or ammonium diuranate, $(NH_4)_2U_2O_7$. The ThO_2 was produced by the extraction of solution from uranium extraction with 40%v/v TBP/kerosene [1].

The filtrated mixed rare earth solution was treated with $BaCl_2$ and H_2SO_4 for removing of radium, Ra (a daughter product of uranium) and precipitated at pH 11 with NaOH. The obtained $RE(OH)_3$ intermediate was leached with HNO_3 at pH 6. The ion exchange process was used to extract and purify Ce, La and other rare earths from the leaching solution [2,3].

Inductively coupled plasma optical emission spectrometry (ICO-OES) and neutron activation analysis (NAA) are the equipment used for the determination of rare earths, uranium, thorium and other associated minerals in the sample during the monazite processing [4]. Although ICO-OES can be simultaneously analyzed rare earths with high sensitivity and more accuracy, it requires digesting of the ore in concentrated acid step and is also suitable for some low concentration rare earths [4,5]. For NAA, this technique suffers from a long irradiation times and long decay times [5]. X-ray fluorescence (XRF) is non-destructive technique for analysis of rare earths, uranium and thorium. It has been reported that this tool could be determined the rare earth, uranium and thorium concentrations in various samples such as mixed REO concentrates, CeO_2 , RE_2O_3 [6], thorium in the presence of uranium [7], monazite processing [8] and phosphate ore [9]. X-ray powder diffraction (XRD) has been applied for identification and quantification the mineralogy as well as crystalline phase structure and composition in various ores etc. monazite and phosphate rock [8,9].

In this work, the wavelength dispersive X-ray fluorescence (WD-XRF) and X-ray powder diffraction (XRD) techniques were developed to study the characterization of uranium, thorium and rare earths in Thai monazite ore processing samples.

MATERIALS AND METHODS

The samples used in this study were the Thai monazite ore, the RE(OH)₃ intermediate, the U₃O₈, the ThO₂, the La₂O₃ and CeO₂ as obtained from the decomposition process of Thai monazite ore by alkali method. All samples were dried at 110 °C for 12 h and then grounded to form fine powder. The chemical and mineralogical analysis of the samples was carried out by using WD-XRF and XRD techniques.

WD-XRF analysis: the sample was mixed with a reagent grade flux (mass ratio of lithium metaborate and lithium tetraborate, 1:4). The ratio of sample and fluxing agent was 1:9. Ammonium iodide as releasing agent was then added. The total amount of mixture was 6.9 g. The mixture was poured into a platinum crucible and fused at 1000 °C for 2 min using a fusion machine (Katanax K2classic automatic fluxer). The sample fused disc was analyzed for uranium, thorium and rare earth elements concentrations using a Bruker S8 Tiger WD-XRF spectrometer.

XRD analysis: the XRD patterns of the samples were performed on a Bruker D8 ADVANCE diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operating at an accelerating voltage of 45 kV and a current of 40 mA. The patterns were recorded in the 2θ range of 10–90° with a 2θ step size of 0.039° and 177 sec/step.

RESULTS AND DISCUSSION

The monazite ore sample was ground to obtain 325 mesh before XRD and WD–XRF analysis. The XRD pattern of the sample showed that the ore consisted of monazite–Ce (Ce, La, Nd)PO₄ with monoclinic structure. All diffraction peaks can be indexed according to the JCPDS card No. 00–046–1295 with lattice constants of $a = 0.6811 \text{ nm}$, $b = 0.7039 \text{ nm}$, $c = 0.6501 \text{ nm}$, $\alpha = \gamma = 90$ and $\beta = 103.54$. The major peaks were observed at $2\theta = 21.63, 25.79, 26.95, 28.78, 29.8, 31.07$ and 34.34 . The average crystallite size of the sample of 38.52 nm was observed. The rare earths including CeO₂ (30.74 wt%), La₂O₃ (11.07%), Nd₂O₃ (10.71 wt%), Y₂O₃ (2.80 wt%), Pr₆O₁₁ (1.84 wt%), Gd₂O₃ (1.15 wt%), Dy₂O₃ (0.51 wt%) and Er₂O₃ (0.14 wt%), ThO₂ (8.89 wt%) as well as UO₂ (0.50 wt%) were detected by WD–XRF.

For the RE(OH)₃ intermediate sample, it has formed after the digestion of monazite ore by alkali method following the separation of thorium and uranium process. The XRD pattern of the sample indicated the presence of cubic of cerium and neodymium oxide with the standard card (JCPDS 00–028–0266). The characteristic diffraction peaks appeared at $2\theta = 28.31, 32.67, 47.05, 55.88, 56.11, 68.67, 75.78$ and 87.72 ($a = b = c = 0.5458 \text{ nm}$ and $\alpha = \beta = \gamma = 90$) with a small crystallite size of 8.13 nm. The concentrations of CeO₂ (65.84 wt%), Nd₂O₃ (14.48 wt%), La₂O₃ (5.97%), Y₂O₃ (3.57 wt%), Pr₆O₁₁ (3.01 wt%), Gd₂O₃ (1.90 wt%) and Dy₂O₃ (0.84 wt%) were found. ThO₂ and UO₂ could not be detected by this WD–XRF technique.

The U₃O₈ sample was obtained by the solvent extraction of Th and U cake with TBP/kerosene extractant. The obtained (NH₄)₂U₂O₇ was calcined at 900 °C to form the U₃O₈ cake. The XRD pattern of the sample exhibited predominantly peaks of uranium oxide at $2\theta = 23.61, 24.97, 25.24, 27.69, 27.96, 34.65, 44.37$ and 46.08 (JCPDS card No. 00–028–0164). The average crystallite size of the sample was 19.00 nm. The WD–XRF result showed that the sample composed of UO₂ (87.77 wt%), ThO₂ (6.21 wt%). The concentration of UO₂ obtained by this WD–XRF agreed well with that determined by XRD technique (UO₂ 87.00%).

After the separation of uranium, the TBP extraction process was used to purify Th and then the ThO₂ cake sample was formed by NaOH precipitation. The sharp characteristic peaks of the sample located at $2\theta = 27.65, 32.01, 45.85, 54.36, 57.01, 66.84, 73.76, 76.02$ and 84.80 can be assigned to cubic phase of ThO₂ which matched well with the standard data (JCPDS card No. 03–065–7222). The lattice parameters were $a = b = c = 0.5596 \text{ nm}$ and $\alpha = \beta = \gamma = 90$ with the average crystallite size of 95.16 nm. The concentration of ThO₂ in the sample was found to be 83.74 wt% with small amount of UO₂ of 0.61 wt%.

The CeO₂ and La₂O₃ containing in the RE(OH)₃ intermediate, were separated and purified by ion exchange process. For CeO₂ sample, all of the diffraction peaks can be indexed to the face centered cubic phase of cerium oxide with lattice constant $a = b = c = 0.5412 \text{ nm}$ and $\alpha = \beta = \gamma = 90$. The sharpness and high intensity of predominant peaks at $2\theta = 28.51, 33.06, 47.44, 56.31, 59.03, 69.37, 76.68, 79.05$ and 88.38 (JCPDS card No. 01–081–0792) indicated the well crystalline nature of the CeO₂ sample. The average crystallite size of the sample was found to be 64.2 nm. The WD–XRF result indicated that the CeO₂ sample contained a 99.47 wt% of pure CeO₂ which matched well with that XRD result.

In case of the La₂O₃ sample, a typical diffraction peaks of La₂O₃ appeared at $2\theta = 27.34, 27.96, 31.62, 35.93, 39.51, 42.15, 48.65, 55.26, 64.00$ and 69.56 (JCPDS card No. 01–076–0572), was observed. The characteristic peaks attributed to hexagonal with lattice parameters of $a = b = 0.6523 \text{ nm}$, $c = 0.3855 \text{ nm}$, $\alpha = \gamma = 90$ and $\beta = 120$ and average crystallite size of 17.16 nm. The La₂O₃ sample analysed by WD–XRF composed of La₂O₃ (89.70 wt%) and CeO₂ (8.15 wt%).

CONCLUSION

Monazite ore found in the tailing of tin from the south of Thailand has been used as source of rare earths, uranium and thorium. The decomposition process using alkali method, solvent extraction and ion exchange techniques were used for separating and purifying those elements. XRD and WD–XRF as fast, accurate and

non-destructive methods were extremely useful for the determination of rare earths, uranium, thorium and associated mineral concentrations in the samples obtained during the process. The elemental compositions of all samples measured by WD-XRF were agreed well with that determined by XRD method. In addition, the concentration of uranium oxide in the U₃O₈ cake sample determined by WD-XRF (87.77 wt%) showed a very good agreement with that obtained by XRD method (87.00 wt%). The same phenomenon was observed for the CeO₂ sample, the CeO₂ concentrations of 99.47 wt% and 99.90 wt% were detected by WD-XRF and XRD, respectively.

REFERENCES

- [1] INJAREAN, U., et al., Batch simulation of multistage countercurrent extraction of uranium in yellow cake from monazite ore processing with 5% TBP/kerosene, *Ener. Proced.* 56 (2014) 129–134.
- [2] RATTANAPHRA, D., et al., Purification process of lanthanum and neodymium from mixed rare earth, *Proc. Pure Appl. Chem. Int. Conf. Thailand*, (2013) 407–409.
- [3] PUSSADEE, C., et al., Purification process and characterization of cerium oxide from mixed rare earth, *Proc. TICHE. Int. Conf. Thailand*, (2012) 142–144.
- [4] BUSAMONGKOL, A., et al., Determination of rare earth elements in Thai monazite by inductively coupled plasma and nuclear analytical techniques, Country Report No. TH-071, IAEA, Vienna (2003).
- [5] ZAWISZA, B., et al., Determination of rare earth elements by spectroscopic techniques: a review, *J. Anal. At. Spectrom.* 26 (2011) 2373–2390.
- [6] WENQI, W., et al., Application of X-ray fluorescence analysis of rare earths in China, *J. Rare Earths* 28 (2010) 30–36.
- [7] TAAM, I., et al., Determination of thorium in the presence of uranium by wavelength dispersive X-ray fluorescence, *Proc. Int. Nucl. Atlant. Conf. Brazil*, (2007).
- [8] TAR, T.A., et al., Study on processing of rare earth oxide from monazite Mongmit Myitsone region, *America. Scient. Res. J. Eng. Tech. Science.* 27 (2017) 43–51.
- [9] ZHANG, Q., et al., Study on the rare earth containing phosphate rock in Guizhou and the way to concentrate phosphate and rare earth metal thereof, *J. Powder Metall. Min.* 3 (2014) 1–4.

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