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Thorium, Uranium and Rare Earth Elements Content In Lanthanide Concentrate (LC) And Water Leach Purification (WLP) Residue Of Lynas Advanced Materials Plant (LAMP)

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Abstract. Lynas Advanced Materials Plant (LAMP) has been licensed to produce the rare earths elements since early 2013 in Malaysia. LAMP processes lanthanide concentrate (LC) to extract rare earth elements and subsequently produce large volumes of water leach purification (WLP) residue containing naturally occurring radioactive material (NORM). This residue has been rising up the environmental issue because it was suspected to accumulate thorium with significant activity concentration and has been classified as radioactive residue. The aim of this study is to determine Th-232, U-238 and rare earth elements in lanthanide concentrate (LC) and water leach purification (WLP) residue collected from LAMP and to evaluate the potential radiological impacts of the WLP residue on the environment. Instrumental Neutron Activation Analysis and γ-spectrometry were used for determination of Th, U and rare earth elements concentrations. The results of this study found that the concentration of Th in LC was 1289.7 ± 129 ppm (5274.9 ± 527.6Bq/kg) whereas the Th and U concentrations in WLP were determined to be 1952.9±17.6 ppm (7987.4 ± 71.9 Bq/kg) and 17.2 ± 2.4 ppm respectively. The concentrations of Th and U in LC and WLP samples determined by γ- spectrometry were1156 ppm (4728 ± 22 Bq/kg) & 18.8 ppm and 1763.2 ppm (7211.4 Bq/kg) &29.97 ppm respectively. This study showed that thorium concentrations were higher in WLP compare to LC. This study also indicate that WLP residue has high radioactivity of ^{232}Th compared to Malaysian soil natural background (63 – 110 Bq/kg) and come under preview of Act 304 and regulations. In LC, the Ce and Nd concentrations determined by INAA were 13.2 ± 0.6% and 4.7 ± 0.1% respectively whereas the concentrations of La, Ce, Nd and Sm in WLP were 0.36 ± 0.04%, 1.6%, 0.22% and 0.06% respectively. This result showed that some amount of rare earth had not been extracted and remained in the WLP and may be considered to be reextracted.

Keywords: Thorium, LC, WLP, REE, NORM.
PACS: 80

INTRODUCTION

Rare earths elements have an important role in many fields of high and green technology and play important role in Malaysia's aspiration to become a high income nation. There is worldwide awareness in the rare earths industry because naturally occurring radioactive material (NORM) is enhanced during the process and creates radiological risks to human health and the environment. In addition, rare earth processing produces large quantities of residue which are disposed rather than being recovered and reused. Some of the rare earth minerals e.g. monazite, exists in nature combined with thorium and its daughter with significant concentrations. Thorium has been producing a radioactive by-product and may represent a significant management challenge. RE residue contains 0.2% Th and has to be stored as a radioactive residue (IAEA, 2011).

Malaysia has had long experience in rare earth industry. There were two rare earths processing plants namely Asian Rare Earth (ARE) and the Malaysian Rare Earth Corporation Plant (MAREC), Papan, Perak, which had been operated until 1992 and closed because of several reasons such as environmental problems and disposal vast amount NORM wastes (Omar 2010; MeorYusoff&Latifah, 2002; ASM, 2013, 2011).

Recently, Lynas Advanced Materials Plant (LAMP) has become one of the largest rare earths processing plant in the world producing rare earth elements (REE) in Gebeng, Pahang. The primary raw material is the lanthanide concentrate (LC) which is imported from Mount Weld mine in Australia and shipped to Malaysia. LC is produced from lanthanide ore after extraction, crushing, and concentration. The plant utilizes physical and chemical treatment processes for REE productions. The annual capacity is

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up to 80,000 tonnes per annum of LC and it produces 22,500 tpa of lanthanide oxide (RIA, 2011).

In principle, lanthanide concentrate contains naturally occurring radioactive material (NORM) 1600 ppm of thorium and 29 ppm of uranium which is enhanced slightly after ore processing(RIA, 2011). The plant generates three types of residues, namely Water Leach Purification (WLP) - synthetic gypsum, Flue Gas Desulphurisation (FGD) and Neutralisation Underflow (NUF). The LAMP produces large volume of WLP (32000 tonnes per year) containing thorium and uranium with concentration of 1655 ppm and 22 ppm respectively (RIA, 2011). NORM is suspected to accumulate in WLP residue after REE extraction. Experimental measurement was studied the deportment of radionuclides and showed that over 99% of thorium and radium in the feed LC will remove to WLP and some uranium will escape to solvent extraction circuit and remove back to WLP residue (RIA, 2011). This residue has become a radiological concern to the authorities and public. WLP residue with significant activity concentration of thorium has been classified as radioactive residue. In the wake of worldwide interest of thorium as an alternative future nuclear fuel, there is a proposal for Th to be separated from RE residue and saved as future nuclear fuel.

The present study determined Th, U and rare earth elements content in lanthanide concentrate (LC) and water leach purification (WLP) residue collected from Lynas Advanced Materials Plant (LAMP) using instrumental neutron activation analysis (INAA) (Ehmann&Vance, 1991; IAEA, 1990) and measured the specific activity of NORM in (LC) and (WLP) residue using low level gamma spectrometry. Evaluation the potential radiological impacts of the WLP residue on the environment will be discussed.

EXPERIMENTAL METHODS

Samples of LC and WLP residue were collected from LAMP. The sampling was carried out by plant's staff. In preparing samples for instrumental neutron activation analysis (INAA), collected samples were thoroughly mixed to obtain homogeneous samples. All representative samples were dried by putting in the oven set at 80^{o}C for 1 day to remove all moisture content for accurate dry weight reporting, crushed to fine powder, thoroughly mixed and homogenised. About0.1 g of each sample, 0.2 g standard reference material (IAEA 312N and IAEA 313B) and 1g of standard solutions were placed in high-purity polyethylene irradiation vials and sealed by heat sealing process. Triplicates were prepared for each sample. Samples, standard reference materials and standard solution were irradiated for 1 hour in the rotary rack (RR) facility of the TRIGA Mark II reactor at Malaysian Nuclear Agency. The measurements were carried out using a HPGe detector (GC3018) with a relative efficiency of 30 % and resolution of 1.8 keV at 1.33 MeV and the analysis of photo peaks were performed using Genie-2000 software (Canberra Inc). The samples were measured for 1 hour at different cooling times, ranging from 2 days to 4 weeks and measured at 4 cm distances from the detector.

In preparing samples for direct gamma spectrometry (HPGe), LC and WLP samples together with standard reference material namely (IAEA soil-375) were dried, sieved, homogenised, and filled in a 250 ml cylindrical container with a weighed amount, sealed hermetically and stored for a minimum period of 4 weeks prior for counting to re-establish the secular radioactive equilibrium between ^{226}Ra and its short- lived daughter products. The specific activities of the natural radionuclides ^{232}Th, ^{238}U, ^{226}Ra and ^{40}K were measured for a period of 12 hours by HPGe γ-ray spectrometry.

The ^{232}Th specific activity was determined from the photopeak of Ac-228 (911.1 keV) and Tl-208 (583.2 keV), the ^{238}U specific activity was assessed using the photopeak of Bi-214 (1764.49 keV), while for ^{226}Ra, its photopeak of Ra-226 (186.26 keV) were identified and ^{40}K was directly determined using its own photopeak 1460.8 keV.

RESULTS AND DISCUSSION

Elemental Concentration

The results of Th, U and rare earth elements concentration in lanthanide concentrate (LC) and water leach purification (WLP) residue samples are presented in Table 1and 2. From the Table1, it's clearly shown that the concentrations of Th in both LC and WLP were high compared to U determined by INAA and direct gamma spectroscopy andcontent of Th in WLP was higher than LC. Basically, Th exists in high content in the ore material and during the processing of LC, Th slightly accumulates in WLP. Most of Th is removed from LC in the beginning stages of LC processing. Through the calcination at temperature up to 600ºC, Th is converted into refractory and insoluble form and disposal into WLP residue (IAEA, 2011).

Moreover, some of rare earth elements were determined in LC and WLP by INAA (see Table 2). It was obvious from the data that the concentration of REE in LC was much higher than in WLP determined for Ce and Nd. This proved that most of REE was extracted during the process of LAMP and some

amount of them was released to WLP which perhaps was considered to be re-extracted.

Natural Radioactivity

The results of ^{232}Th, ^{238}U, ^{226}Ra, and ^{40}K in LC and WLP samples are presented in Table 1. The activity concentrations of ^{232}Th in LC and WLP obtained was 4728 ± 22 Bq/kg and 7211.4 Bq/kg which the highest concentrations compared to ^{238}U 234.3 ±11.5 Bq/kg and 372.9 Bq/kg. This study showed that thorium concentrations values were higher in WLP compare to LC and alsoWLP residue has high radioactivity of ^{232}Th compared to Malaysian soil natural background (63 – 110 Bq/kg)(UNSCEAR, 20009). WLP residuewas classified as radioactive residue, come under preview of Act 304 and regulations. From the safety reports and standards(IAEA, 2006;2011),material containing radionuclides of natural originwithactivity concentration below values 1 Bq/g for uranium and thorium series radionuclides and 10 Bq/g for ^{40}K are usually unnecessary to regulate. If the activity concentrations levels in materials are exceed the mentioned values, materials cannot be released from regulatory control. It can be seen from the obtained results that activity concentrationof Th is 7.2 and 4.7Bq/g in WLP and LC.

According to many investigations (Ismail et al., 2011;Oatway et al., 2004), NORM wastes or residue have long term radiological impact and require appropriate controls of workers, public and the environment safety. Occupational and public radiation exposure will increase if the activity concentrations of NORM in rare earth residues increase too. Potential radiological hazards from thorium and its daughters Radium-228 and Ra-224 will take place therefore, disposal those residues in properly and safely ways is required.

TABLE 1. Elemental concentration (ppm) of Lanthanide Concentrate (LC) and Water Leach Purification (WLP) residue of Lynas Advanced Materials Plant (LAMP) by INAA and γ- ray spectrometry

Element	LC		RSD %	RIA report°	WLP		RSD %	Relative error %	RIA report°	*Malaysian soil (Bq/kg)
	HPGe	INAA			HPGe	INAA				
Th	1156 (4728 ± 22 Bq/kg)	1289.7 ± 129	10.0	1600 (5700 Bq/kg)	1763.2 (7211.4 Bq/kg)	1952.9 ±17.6	0.9	9.2	1655 (5980 Bq/kg)	63 - 110
U	18.8 (234.3 ±11.5 Bq/kg)	-	-	29 (300 Bq/kg	29.9 (372.9 Bq/kg)	17.2 ± 2.4	13.6	11.8	22 (230 Bq/kg)	49 - 86
Ra-226	148.1± 12.4 Bq/kg	-	-	-	229.1 Bq/kg	-	-	-		38 - 94
K-40	386.8± 10.1 Bq/kg	-	-	-	602.5 Bq/kg	-	-			170 - 430

* (UNSCEAR ,2000)

°Radiological impact Assessment (RIA) of Lynas Advanced Materials Plant: Executive Summary, Rev 4, November 2011(RIA, 2011).

TABLE 2. Elemental concentration (%) of REE in Lanthanide Concentrate (LC) and Water Leach Purification (WLP) residue of Lynas Advanced Materials Plant (LAMP) by INAA.

Element	LC	RSD %	WLP	RSD %
La	-		0.36 ± 0.04	10.7
Ce	13.2± 0.6	4.6	1.6± 00	0.1
Nd	4.7± 0.1	2.7	0.22± 00	0.7
Sm	-		0.06± 00	10.7

CONCLUSION

Th, U and rare earth elements content in LC and WLP residue from LAMP was determinedusing INAA and γ-spectrometry. Thorium concentrations values were higher in WLP compare to LC and also WLP residue has high radioactivity of ^{232}Th (7.2Bq/g) compared to Malaysian soil natural background. Therefore, regulatory control is recommended, as long term radiological impact will take place because of the Th concentration above 1Bq/g. The Lynas residue could be used as raw materials for other industries if concentrations of the thorium and uranium were to be reduced to natural concentration. Otherwise, permanent, safe and secure repository site should be provided. Thorium content in the residue can be saved for future nuclear fuel after many stages of radiochemical separations to be done. From the present study, is recommended that more researches and investigations in WLP and rare earth residue are needed.

REFERENCES

1. International Atomic Energy Agency (IAEA), Radiation Protection and NORM Residue Management in The Production of Rare Earths from Thorium Containing Minerals, *Safety Reports Series* **68** (2011).
2. M. Omar, NORM Processing in Malaysia: An overview nuclear Malaysia /L/2010/11.1, 2010.
3. M. S.Meor Yusoff, A. Latifah, Rare earth processing in Malaysia: case study of ARE and MAREC plants, *Proceedings of Regional Symposium on Environment and Natural Resources* **1**, 10-11 April, Kuala Lumpur, 2002, pp. 287-295.
4. The Academy of Sciences Malaysia (ASM), "Revitalising of rare earth mineral programme in peninsula Malaysia as a strategic industry" in *The Academy of Sciences Malaysia (ASM) study report* 1/2013(2013).
5. The Academy of Sciences Malaysia (ASM), Rare earth industries: moving Malaysia's green economy forward, A report by The Academy of Sciences Malaysia & The National Professors' Council (2011).
6. Radiological impact Assessment (RIA) of Lynas Advanced Materials Plant: Exective Summary, Rev 4, Novmber 2011(2011).
7. International Atomic Energy Agency (IAEA), Practical aspects of operating a Neutron Activation Analysis Laboratory, *IAEA- TECDOC*-**564**,1990.
8. W.D. Ehman, D.E. Vance, Radiochemistry and Nuclear Methods of Analysis, New York, NY: John Wiley and Sons, 1991.
9. UNSCEAR 2000 REPORT*, Exposures from Natural Radiation Sources.* Vol. 1 pp 74
10. International Atomic Energy Agency, Assessing the Need for Radiation Protection Measures in Work Involving Minerals and Raw Materials, *Safety Reports Series* No. 49, IAEA, Vienna (2006).
11. B. Ismail, I. L Teng, Y. M. Samudi, Relative Radiological Risks Derived from Different TENORM Wastes in Malaysia, *Radiation Protection*, 2011.
12. W.B. Oatway, J.A. Jones, P.V. Shaw, S.F. Mobbs, Radiological Impact on the UK Population of Industries which use or Produce Materials Containing Enhanced Levels of Naturally Occurring Radionuclides: Zircon Sands Industries, *IAEA-TECDOC*-**1472**. Naturally Occurring Radioactive Materials (NORM IV),2004.
13. http://www.unscear.org/docs/reports/annexb.pdf. (30 July 2013)