

DIGESTION STUDY OF WATER LEACH PURIFICATION (WLP) RESIDUE FOR POSSIBILITY OF THORIUM EXTRACTION

(Kajian Penghadaman Residu Pemurnian Larut Resap Air (WLP) Untuk Kebarangkalian Pengekstrakan Torium)

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Abstract

Water leach purification (WLP) is the main residue being produced by Lynas Advanced Materials Plant (LAMP). During rare earths elements extraction process, thorium is removed completely to WLP. The objective of this study was to extract thorium from WLP in order to reduce the level of radioactivity and to store Th for future nuclear fuel. Alkali and concentrated acids process was used to recover the Th from WLP. The concentration of Th and U in WLP was determined by Instrumental Neutron Activation Analysis (INAA) and found to be 1952.9 ± 17.6 mg/kg and 17.2 ± 2.4 mg/kg respectively. Digestion process of WLP via sodium hydroxide, concentrated nitric and sulphuric acids using different time and temperature has been tested. The Th concentrations in liquid phase were determined by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). In both processes less than 5% recovery of Th has been achieved. This study showed that very low Th recovery was achieved due to thorium was probably converted into refractory and insoluble form through the calcination stage of LAMP processing. Therefore different techniques should be used to recover the thorium.

Keywords: thorium, digestion, WLP, Th recovery

Abstrak

Pemurnian Larut Resap Air (WLP) merupakan residu utama yang dihasilkan oleh *Lynas Advanced Materials Plant* (LAMP). Semasa proses pengekstrakan unsur nadir bumi, torium telah dikeluarkan sepenuhnya kepada WLP. Objektif kajian ini adalah untuk mengekstrak torium daripada WLP dalam usaha untuk mengurangkan aras radioaktiviti dan penyimpanan torium untuk bahan api nuklear. Kepekatan Th dan U dalam WLP telah ditentukan melalui Analisis Pengaktifan Neutron (APN) dan didapati kepekatan masing – masing adalah 1952.9 ± 17.6 mg/kg dan 17.2 ± 2.4 mg/kg. Proses penghadaman WLP telah diuji menggunakan natrium hidroksida, asid nitrik pekat dan asid sulfurik pekat pada masa dan suhu yang berbeza. Kepekatan Th dalam fasa cecair telah ditentukan menggunakan Induktif Plasma Pasangan– Spektroskopi Jisim (ICP-MS). Dalam kedua- dua proses pemulihan, didapati kurang daripada 5% Th telah ditemui. Kajian ini menunjukkan bahawa penemuan Th adalah sangat rendah kerana torium mungkin telah ditukar kepada bentuk refraktori/ tahan panas dan tidak melalui peringkat pengklasinan dari pemprosesan LAMP. Oleh itu, teknik yang berbeza perlu digunakan untuk mendapatkan torium.

Kata kunci: torium, penghadaman, WLP, mendapatkan Th

Introduction

Thorium- based nuclear fuel has been special interested in nuclear energy recently and in the near decade thorium will be the essential future nuclear fuel [1, 2, 3, 4, 5]. Thorium is the most abundant natural radioactive element, 8 ppm in earth crust and three times abundant in nature compared to uranium. Soil commonly contains thorium in the range of 3.4 –10.5 mg/kg. Th concentration in natural water is extremely low: 1.5 ng/l in sea water and less than 1 ng/l in ground water because its compounds solubility is very low [6]. The highest known world thorium resource is estimated in United States (440,000 tonnes), Australia (300,000 tonnes) then, India (290,000 tonnes) and

Malaysia has 0.4% of thorium world resources (4500 tonnes) [7]. Primary source of thorium is the rare-earth and thorium phosphate mineral- monazite (Ce, La, Nd, Th) PO_4 which contains 2.5% of thorium. Thorium occurs in various minerals including thorite (ThSiO_4) and thorianite (ThO_2), can be associated with several other minerals and also is a by-product in rare-earth production industry [8, 9].

Extraction of thorium from different matrix has been achieved for a century using all types of separation techniques. Typically, thorium is extracted from its minerals with either hot sulphuric acid or hot alkali, converted to thorium nitrate and extracted from impurities with organic solvent using tributyl phosphate TBP in kerosene [10, 11, 12]. Nitrates and chlorides of thorium in acid solutions are widely used to extract thorium into organic solvents. The basis of the separation and purification of thorium depends on the solubility of thorium in water and organic solvents. Due to thorium chemistry such as low solubility, researches on thorium are still being carried out [6]. In general thorium compounds are water insoluble, with the exception of the nitrate, sulfate, chloride, and perchlorate. Thorium is a by-product of Lynas Advanced Materials Plant (LAMP) which is processing the rare earth ores (lanthanide concentrate) to produce rare earth elements. About 32000 tonnes per year of Water Leach Purification (WLP) is generated by the plant as well as two other types of residue i.e Flue Gas Desulphurisation (FGD) and Neutralisation Underflow (NUF). WLP residue contains thorium and uranium with concentration of 1655 ppm and 22 ppm respectively [13] and it can be estimated that Lynas will produce about 53 tonnes per year of Th in WLP. Sulphuric acid digestion process is used to digest lanthanide concentrate at 650°C for 2.5 hours in a stirred reactor. During the digestion most of Th, rare earth elements and U go into the solution with sulfate and phosphate anions. Because of the chemical similarity between thorium and lanthanides cations in solution selective precipitation is used to separate Th from rare earth elements.

According to Lynas report, over 99% of thorium in the feed lanthanide concentrate is removed to WLP and through the calcination at temperature up to 600°C, Th is converted into refractory and insoluble form and disposal into WLP residue [13, 14]. From fundamental chemistry of Th, solubility of Th is very little when the pH is above 1. During the calcine leaching stage at 650 °C in LAMP process, Th is completely precipitated probably as thorium pyrophosphate (ThP_2O_7) when pH of the leach solution was adjusted to 3.5 by addition MgO [13]. Thorium pyrophosphate, iron and a few other heavy metals, with other insoluble matter such as barium sulphate, calcium sulphate and silica are all together constituted WLP residue [14].

In the view of the best matrices storage for Th radioactive waste materials, thorium phosphate compounds is chosen due to their radiation resistance and low solubilities [11].

The purpose of this research is to find out the possibility of thorium extraction from WLP residue using alkali and acid digestion process and produce thorium nitrate which is the best form for solvent extraction. Research on separation and purification of Th from RE residue can also reduce the level of radioactivity in the residue and obtain high –purity Th for saving future nuclear fuel.

Materials and Methods

Determination of Th and U in WLP samples

The WLP residue sample was collected from LAMP and treated to produce fine powder. Instrumental Neutron Activation Analysis (INAA) was employed to determine the concentration of Th and U in WLP. In INAA analysis, Standard reference materials used were IAEA 312N and IAEA 313B. About 0.1 g of WLP sample, 0.2 g of standards were placed in high-purity polyethylene irradiation vials and sealed by heat sealing process. Triplicates were prepared for each sample. Samples, standard reference materials 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 counted at 4 cm distances from the detector.

Chemical processing of WLP

Sodium hydroxide, nitric acid and sulphuric acid were used in the digestion of WLP. The digestion experiments were performed using the glass beakers and a crucible on the stirring hot plate. Various molarities of sodium

hydroxide, concentrated nitric and sulphuric acids, different digestion temperatures and digestion times were employed to establish optimum digestion conditions.

In the alkaline processing, about 2 g of fine powder residue was treated with an aqueous solution of sodium hydroxide having a concentration about 73% and 40% by weight under constant stirring (600 rpm) at a temperature about 150°C and under constant digestion time (2 hours). Whereas, the ratio by weight of sodium hydroxide/ WLP residue about 1 was digested in a crucible for 45 min at 130 °C. The produce mass was dissolved in concentrated nitric acid and the filtrate solution was prepared for Th determination via ICP-MS [11, 10, 15]. On the other hand, acid digestion of WLP was carried out using concentrated nitric and sulphuric acid, at different temperatures, time and stirring. The product filtrate solutions were prepared for Th analysis.

Determination of Th in filtrate samples

The Th content in the filtrate solutions obtained from alkaline and acid digestion was determined using ICP-MS. The ICP-MS instrument used was an ELAN 9000 (PerkinElmer SCIEX). Prior to ICP-MS analyses, standard solution was prepared using PerkinElmer Pure Plus (multi-element calibration standard 2). Concentration of Th was calculated from the measurement of standard solutions and filtrate after WLP digestion process. The recovery of thorium was calculated from concentration of Th in the initial WLP samples and concentration of Th in filtrate sample. The recovery of thorium will indicate the efficiency of digestion process and dissolution of Th compound existing in the WLP. The scheme for proposed NaOH digestion of WLP and recovery of Thorium shown in Figure 1.

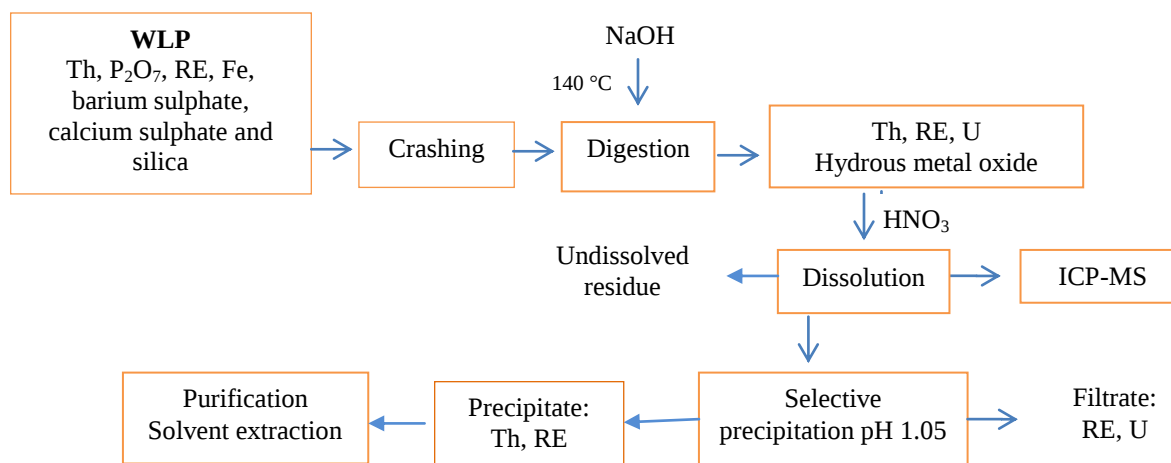


Figure 1: Simplified Scheme for Proposed NaOH Digestion of WLP and Recovery of Thorium

Results and Discussion

Determination of Th concentration in WLP residue was done before carrying out the alkali and acid digestion. Table 1 shows the concentration of Th and U in WLP residue determined by INAA. Th concentration in residue was 1952.9 ppm (7.98 Bq/g) which was higher than 1 Bq/g therefore; it needs to be considered for regulatory control as the radioactive residue. Rare earth ore reacted with sulphuric acid process according to the following reaction (1) and (2):



The temperature should be kept below 230 °C otherwise formation of water insoluble thorium pyrophosphate (ThP_2O_7) will take place by converting the sulphate of thorium while the rare earth sulphates remain stable in sulphate solution [14,16]. In LAMP process, about 650°C is used to digest the rare earth ore with concentrated sulphuric acid. The reaction product is leached in water followed by reduction of acidity and the filtration produces a rare earth sulphate solution and a filter cake containing thorium pyrophosphate which is the most important content in WLP. This study and experiments based on the fact that chemical form of thorium is pyrophosphate as mentioned by Lynas.



Theoretically, Thorium pyrophosphate reacts with sodium hydroxide as the equation (3), the resulted water insoluble Th hydroxide was dissolved with nitric acid to produce soluble Th nitrate. In practical, WLP was digested with sodium hydroxide which was expected to dissolve thorium pyrophosphate and concentrated nitric and sulphuric acids were also used for digestion of WLP. The concentrations and recovery of Thorium after WLP residue digestion via sodium hydroxide and concentrated acids digestion are presented in Table 2.

It is obvious that by using different digestion approaches either alkali or acids have given less than 5% for Th recovery i.e in the range between 0.17 and 4.99 % because of the undissolved chemical form of Th. Digestion using strong NaOH solutions 73% by a weight ratio of sodium hydroxide/ WLP about 7 was relatively recovered Th much compare to NaOH 40% or NaOH (1:1) solid. The best result from digestion was used concentrated nitric acid at 70 °C for 1.5 h and the weight ratio of nitric acid/WLP about 10. Changing type of acids with similar conditions; don't increase the recovery of Th. It is likely that Th is converted to refractory and insoluble form in Lynas process which is difficult and not possible to dissolve by strong alkaline solutions or concentrated acids.

Table 1: Elemental concentration (ppm) of Th and U in Water Leach Purification (WLP) residue of LAMP by INAA

Elements	WLP	RSD %	Relative error %
Th	1952.9 ± 17.6	0.9	9.2
U	17.2 ± 2.4	13.6	11.8

Table 2: Concentrations and recovery of Thorium after WLP residue digestion via sodium hydroxide and concentrated acid digestion

Digestion method	T (°C)	Time (hours)	Weight ratio	Stir rpm	Concentration ppm (ICP-MS)	Recovery %
NaOH 73%	140	2	7 (soda/WLP)	600	25.71	1.32
NaOH 40%	150	2	4 (soda/WL)	600	14.35	0.73
NaOH (s:s)	130	0.75	1 (soda/WLP)		3.41	0.17
HNO ₃ 65%	70	1.5	10 (acid/WLP)	600	97.45	4.99
HNO ₃ 65%	130	2	10 (acid/WLP)	400	28.78	1.47
H ₂ SO ₄ 98%	210	3	18 (acid/WLP)	450	29.99	1.54

Conclusion

Proposed digestion process has been tried to extract Th from WLP residue. Different digestion methods were used such as sodium hydroxide, concentrated nitric and sulphuric acids with various temperatures and time to obtain a good recovery of Th. The digestion process has recovered very low Th in the range of 0.17- 4.99 %. The recovery percentage was very less than it was expected. It can be concluded that thorium was probably converted into refractory and insoluble form through the calcination stage of LAMP processing and it was difficult to recover it by strong sodium hydroxide or concentrated nitric and sulphuric acids. Perhaps different techniques should be studied to recover thorium. Further researches and investigations on WLP residue and rare earth residue are recommended and possibility of separation Th from RE residue will reduce the level of radioactivity in the residue as well as obtain high –purity Th which will be store for future nuclear fuel usages.

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