Estimation of Worker's Exposure to Thorium from Lanthanide Concentrate and Water Leach Purification Residue via Ingestion

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I. Introduction

Thorium is a radioactive element occurring naturally in low concentrations (about 10 ppm) in the earth's crust (HPS, 2014). Small amount of thorium found in soil is harmful when exposed to human. It is harmful to humans, who can be exposed to the small amounts found in the soil(EPA, 2014). Higher level of ^{232}Th radionuclides are present in geological material such as monazite sand. Essentially all naturally occurring thoriums are presented as ^{232}Th radionuclide and ^{230}Th radionuclide. ^{230}Th radionuclide is a radioactive decay product of ^{238}U radionuclide which can be found at low concentration in uranium deposits and mill tailings (HPS, 2014).

In 2012, the Malaysian government awarded Lynas Advanced Material Plant (LAMP) license to process rare earth elements (MOSTI, 2012). Lanthanide concentrate (LC) is transferred into the Advanced Materials Plant where it is subjected to the cracking and separation process involving concentrated acid in a rotary kiln and water leaching of the calcine. These processes are followed by three stages of leaching and solid-liquid. In separation process, solvent extraction will be used to separate, purify and concentrate the lanthanide elements. The lanthanide elements are finally precipitated and calcined to produce a range of carbonate and oxide products. After that, three separate residues are produced known as Flue Gas Desulphurisation (FGD), Neutralisation Underflow (NUF) and Water Leach Purification (WLP). WLP is the main residue produced by LAMP the extraction process of leaching and purifying the water soluble lanthanide components of calcined and cracked lanthanide concentrate(MOSTI, 2012). It also have the highest radionuclide and toxic content than NUF and FGD(Schüler et al., 2011).
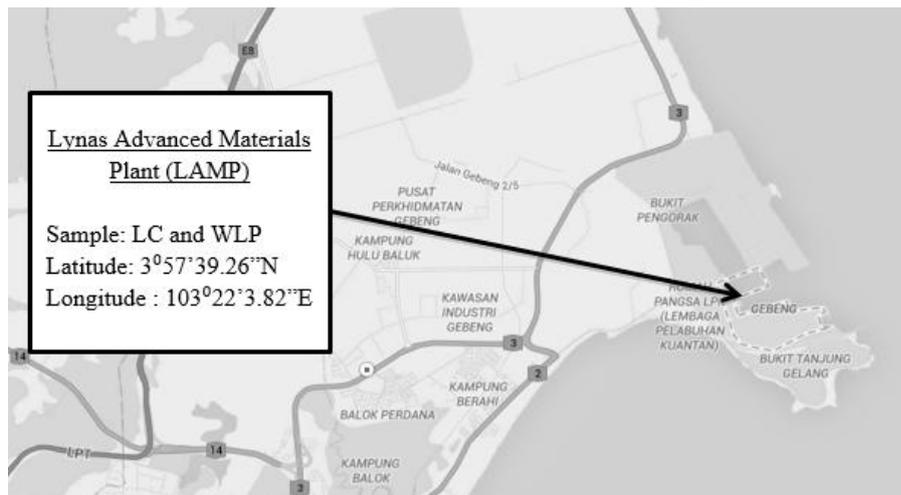
Lanthanide concentrate and WLP can enter the human digestive system either directly or (indirectly)via contaminated soil.The thorium radionuclide, ^{232}Th, may enter the human digestive system via intentional or accidental intake of (contaminated) soil. Intake of LC and WLP may inadvertently occur through consumption of food contaminated with soil, via either inhalation or swallowing of dust suspended in the air, or directly from hand-to-mouth (particularly by children, when playing with soil)(Stanek and Calabrese, 2000). Living near a thorium contaminated site, or working in an industry where thorium is widely used, increases the probability of thorium exposure (EPA, 2014). Because of the radioactive natureof ^{232}Th, this exposure can be a radiation hazard for workers. The increase of ^{232}Th radionuclide in soil can occur either through uncontrolled mineral mining activities involving ^{232}Th radionuclide, in addition to the leakage of radionuclides from the nuclear industry, such as rare earth processing plant or a nuclear accident that can cause pollution to human and environment (Arogunjo et al., 2009). When inhaling or ingesting ^{232}Th radionuclide, it will be accumulated in human lungs, liver and skeleton tissues. Deposition of large quantities of ^{232}Th radionuclide in particular organs produce radiation damages, biochemical and morphological changes. This results in weakening of immune systems, developingvarious types of disease/cancers and increase mortality rate (Abbady, 2004).

This study is aimed to investigate and measure human exposure to ^{232}Th radionuclide derived from LC and WLP that enters the human digestive system in a simulated human digestive system for both adults and children. It is primarily focused on ^{232}Th radionuclide found in LC and WLP. The objectives of this study are to determine the level of ^{232}Th radionuclide solubility in LC and WLP and to analyse the effectiveness of ^{232}Th radionuclide solubility with synthetic gastrointestinal fluids using US P *in vitro* digestion method.

II. Methodology

2.1. Study area

This study has been carried out in Lynas Advanced Materials Plant (LAMP), Gebeng, Pahang. The sampling locationis shown in Fig. 1. Standard soil sample IAEA SOIL-312 (Valkovic et al. 1992)used as a reference standard in this study.

2.2. XRF method

X-Ray Fluorescence Spectrometer (XRF) was used in this study to determine the concentration of [232]Th radionuclide before ingestion method was carried out. The LC and WLP sample was dried, filtered and sieved to be refined until 1.0g of sample was obtained. Later, all the samples were turned into pellet with a ratio of 1 : 6 of 1.0 g of sample and 6.0g of ascorbic acid. Finally, the pellets were labeled and analysed using XRF. The performance of instrument was assessed by comparing XRF analysis result with the standard soil sample, IAEA SOIL-7 (Pszonicki et al. 1984).
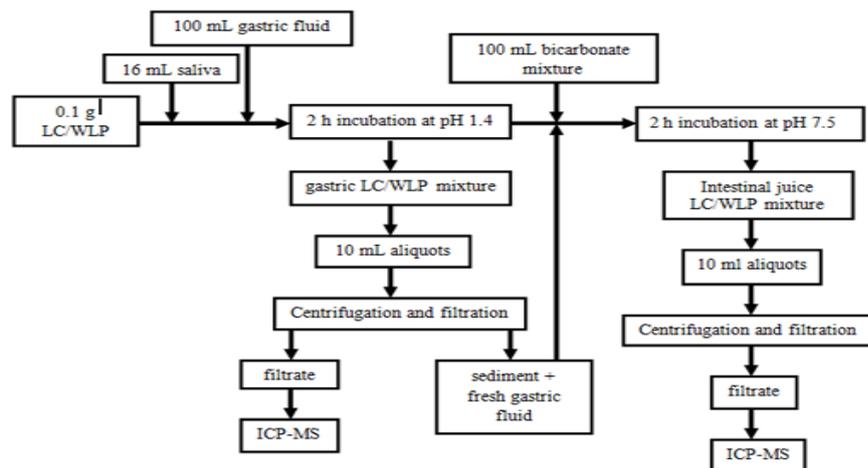
2.3. US P method

The method described per the US Pharmacopia (US P) iswas used to determine the bioaccessibility of heavy metals in the stomach from contaminated soils using a synthetic gastric solution, originally developed based on Hamel et al. (Hamel et al., 1998)experiment which currently used to determine the bioaccessibility of heavy metals in the stomach from contaminated soils using a synthetic gastric solution. The methodology uses the US P Simulated Gastric Fluid (NaCl, HCl and pepsin) to extract the [232]Th radionuclides at 37 ºC for two hours. Table 1 shows the preparation of saliva, gastric fluid and intestinal fluid. This method includesa simulated digestive tract method "intestinal phase" and a simulated gastric extraction method "gastric phase".

Table 1 Preparation for the saliva, gastric fluid and intestinal fluid.

Saliva		Gastric Fluid	
Sodium Chloride (NaCl)	0.4 g	Sodium Chloride (NaCl)	2.0 g
Potassium Chloride (KCl)	0.4 g	Pepsin	3.2 g
Calcium Chloride (CaCl$_2$ $_X$ 2H$_2$O)	0.6 g	Hydrochloric Acid 30% (HCl)	7.0 ml
Magnesium Chloride(MgCl$_{2X}$ 6H$_2$O)	0.96 g		
Mucin	4.0 g		
Urea	1.0 g	Urea	1.0 g
Final pH	5.5	Final pH	2.0
Intestinal Fluids			
Sodium Bicarbonate (NaHCO$_3$)		16.8 g	
Final pH		7.5	

These methods are generally run at the temperature of 37^{0}C, but the extraction time, pH and particular composition of the respective simulated digestive fluids are varied (Wragg and Cave, 2003). Fig. 2. shows the sequence of US P method. Both LC and WLP were prepared for this experiment. The filtered concentrations of [232]Th radionuclides was measured by inductively coupled plasma mass spectrometry (ICP-MS).

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100 mL gastric fluid

16 mL saliva                              100 mL bicarbonate
                                          mixture

0.1 g
LC/WLP          →  2 h incubation at pH 1.4        2 h incubation at pH 7.5

                   gastric LC/WLP mixture          Intestinal juice
                                                   LC/WLP mixture

                   10 mL aliquots                  10 ml aliquots

                   Centrifugation and filtration   Centrifugation and filtration

                   filtrate     sediment +         filtrate
                                fresh gastric
                   ICP-MS       fluid              ICP-MS
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The concentration of ^{232}Th radionuclide was calculated based on the following equation:

$$\rho = \frac{c \cdot M}{V} \qquad (1)$$

where ρ is the sample concentration (mg/kg), c is the mean of the sample from the ICP-MS analysis (ppb), V is the volume of the sample in this experiment and M is the mass of the sample.

The value of committed effective dose and the committed equivalent dose was calculated by using equation as follows:

$$H_A = \Sigma_{Th} I_{ATh} h_{ATh} \qquad (2)$$

Where H_A is thecommitted effective dose or the committed equivalent dose (Sv) by ingestion, I_{ATh} is the activity (Bq) of ^{232}Th radionuclide in samples (Bq/kg), h_{Aj} is the ingestion dose coefficient (Sv/Bq) for the effective dose or for the target organs for ^{232}Th radionuclides. Based on IAEA 1999, given the committed effective dose for ^{232}Th radionuclide is 0.23μSv/Bqand committed equivalent tissue dose per unit activity ingested by adults are 0.7μSv/Bq for bone surfaces,0.78μSv/Bqfor kidney and 0.74 μSv/Bqfor liver(IAEA, 1999).

The mortality cancer risk was estimated by using equation as follows :

$$ELCR = A_{ir} \cdot A_{is} \cdot R_c \qquad (3)$$

Where A_{ir} is the annual intake of ^{232}Th radionuclide in the sample (Bq), A_{is} is the average span of life (74 years) and mortality risk coefficient (Bq^{-1}) of the sample(Asaduzzaman et al., 2015).
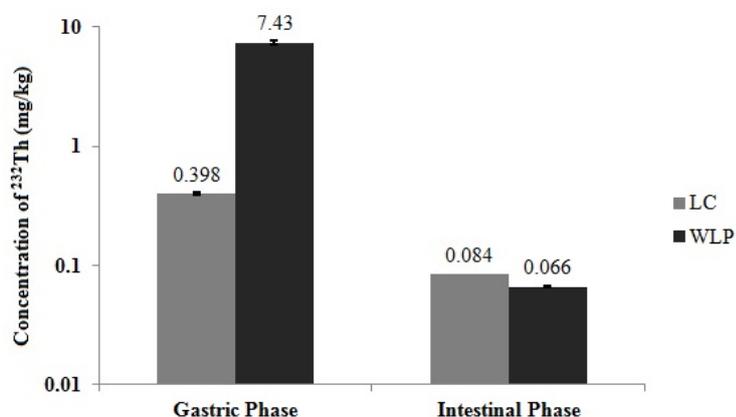
III.   Results and discussion

The concentrationsof ^{232}Th radionuclide determinated by XRF andICP-MS aresummarizes in Table 2. X-ray fluorescence (XRF) spectrometry analysis shows that WLP had the highest concentration of ^{232}Th radionuclide (27.0 mg/kg) followed by LC (18.0 mg/kg). This represents the concentration of^{232}Th radionuclide before ingestion.The ^{232}Th radionuclide in the LC sample was break down after cracking and leaching process.^{232}Th radionuclide in the WLP sample was more soluble than that in the LC sample. The WLP process will generated the most radioactive and contaminated tailings by producing heavy elements such as thorium and uranium(Mehta and Monteiro, 2006).In addition, the concentration of ^{232}Th radionuclide in LC and WLP before undergoing the digestive tract method analysis was found to be dependents on soil origin and process(NTN, 2012).

Table 2 Concentration of ^{232}Th radionuclide before and after ingestion method.

Sample	XRF	Solubility of ^{232}Th radionuclide (ICP-MS)		Specific Activity of ^{232}Th radionuclide (ICP-MS)	
		Gastric Phase	Intestinal Phase	Gastric Phase	Intestinal Phase
	(mg/kg)	(mg/kg)	(mg/kg)	(Bq/kg)	(Bq/kg)
LC	18.0	0.398 ± 0.007	0.084 ± 0.000	1.616 ± 0.028	0.341 ± 0.000
WLP	27.0	7.430 ± 0.214	0.066 ± 0.001	30.166 ± 0.869	0.268 ± 0.004

Fig.3,shows that the concentration of ^{232}Th radionuclide from the WLP samples was highest in the gastric phase (7.43±0.21 mg/kg) and decreased during the intestinal phase (0.0657±0.001 mg/kg). The concentration of ^{232}Th radionuclide from LC samples was 0.398±0.007 mg/kg in the gastric phase and 0.084±0.001 mg/kg in the intestinal phase. The decreaseswerecaused by different pH values of the synthetic gastric fluid and synthetic intestinal fluid,with an increased concentration of ^{232}Th radionuclide in gastric phase,which has more acidic.Furthermore, the specific activity of ^{232}Th radionuclide for WLP was highestin the

gastric phase (30.166 ± 0.869 Bq/kg) and decreased in the intestinal phase (0.268 ± 0.004 Bq/kg). However, thespecific activity for LC increased in the intestinal phase: 1.616 ± 0.028 Bq/kg vs. 0.341 ± 0.000 Bq/kg in the gastric and intestinal phase, respectively.

According to Oliver et al. (Oliver et al., 1999), lowering the pH of the synthetic gastric fluid increases the solubility of trace elements. This leads to ^{232}Th radionuclide being dissolved in acid by means of a chemical reaction(Jernström et al., 2002). Additionally, ^{232}Th radionuclide reacts chemicallyin acidic than in alkaline conditions. According to Lynas report, in the refining process ofover 99% of ^{232}Th radionuclide is removed from LC to WLP and through calcination at temperature up to 600^0C, ^{232}Th is then converted into refractory and insoluble forms and disposed into WLP residue. A fundamental chemical property of ^{232}Th poor solubility at a pH greater than 1 (AL-Areqi et al., 2014).Thedecreases in soluble concentrations of ^{232}Th radionuclides in LC and WLP during the intestinal phase could be because of chemical precipitation at pH 7.5, and the formation of less soluble or insoluble ^{232}Th compounds because of absorption by soil minerals, organic material and other suspended solids (Höllriegl et al., 2010).

According to the Washington State Department of Health (WSDH, 2002), the level of daily intake of ^{232}Th radionuclide in the form of food or liquid is 3 mg kg^{-1}. We found the concentration of WLP residue in the intestinal phase, which is the site at which ^{232}Th is absorbed into human bloodstream, to be significantly lower than the value referred in the guideline by Washington State Department of Health (WSDH, 2002).

The maximum concentration of ^{232}Th radionuclide in the intestinal phase for high risk cases was 0.084 mg/kg (Table 2). The daily intake of ^{232}Th radionuclide is 0.021 mg/kg/day.Calculating from this value, about 4.2 µg/kg/day of soluble ^{232}Th radionuclide will enter the human blood stream. This is below the minimum risk level (of 3 mg/kg/day). Thus, the concentrations of ^{232}Th,based on these *in vitro* extraction techniquesare considered safe.

The specific activity of ^{232}Th radionuclide in this study for high risk casesis 0.3410 Bq/kg. Thus, thecommitted equivalent dose of ^{232}Th radionuclide is 2.387 x 10^{-3} µSv on the bone surface,2.660 x 10^{-5} µSv in the kidneyand 2.523 x 10^{-5} µSvin the liver. The estimated annual committed effective dose of ^{232}Th radionuclide is1.718 x 10^{-2}µSvwhich is lower than the annual doses (20 mSv) recommended by the Strategies and Methods for Optimization of Internal Exposures (SMOPIE) project's occupational exposure guidelines for rare earth element processing(UNSCEAR, 2000). Thus, the resultswasinthe permitted level and safe without posing any significant radiological threat towards population.However, the level of exposures depends on a number of factors, including the type of mine, the geology and the working conditions, particularly the ventilation (UNSCEAR, 2000).

According to Sathyapriya et al. (Sathyapriya et al., 2012), about 0.02 to 0.05% of the ingested ^{232}Th is absorbed into the bloodstream via theintestines tracts. ^{232}Th radionuclide which enters the human body will accumulate inside the lungs, liver and bones. Of that, about 70 % is deposited in the bone, where it is retained with a biological half-life of about 22 years, 4 % is deposited in the liver where it is retained with a biological half-life 700 years and 16 % is uniformly distributed to all the other organs and body tissues, where it is cleared with a biological half-life of 700 years (according to simplified models that do not reflect intermediate redistribution)(Sathyapriya et al., 2012). The remaining 10 % eliminated in urine via the kidneys(ATSDR, 1990).

In this study, the risk ofmortality fromcancer was1.354 x 10^{-4}. This gives an annual probability of death 1.0 x 10^{-4};lower than than acceptable lifetime cancer risk limit of 1.0 x 10^{-3} for general radiological risk (Patra et al., 2013). Studies have shown that inhalation of thorium dust increases the risk of developing both lung and pancreatic cancer. The risk of bone cancers is also increased because thorium may be stored in the bones.

By natural processes, [232]Th radionuclide is transferred toother living beings viavarious paths. These need to be monitored and potential hazards need to be assessed. Environmental studies are generally conducted to trace the pathway of radionuclide/radiotoxic elements that affect living beings. However, environmental monitoring and meaningful interpretation of data from manmade pollution are made complicated if adequate knowledge exists about the natural abundance of radioactive elements in the environment (El-Taher et al., 2005).

IV. Conclusions

The concentration of [232]Th radionuclide from the WLP samples was found to be highest during the gastric phase (7.43 ± 0.21 mg/kg) and decreased during the intestinal phase (0.066 ± 0.001 mg/kg). Similarly, the concentration of [232]Th radionuclide from theLC samples was greater during the gastric than during the intestinal phase(0.398 ± 0.007 mg/kg and 0.084 ± 0.001 mg/kg, respectively). The decrease is caused by the differences of pH value of synthetic gastric fluid and synthetic gastrointestinal fluid.The committed equivalent doses from assessment of the bone, kidney and liver were $2.387 \times 10^{-3} \mu Sv$, $2.660 \times 10^{-5} \mu Svand2.523 \times 10^{-5} \mu Sv$, respectively. The annual committed effective dose of [232]Th radionuclide was $1.718 \times 10^{-2} \mu Sv$.The lifetime cancer risk because of [232]Th radionuclide exposure was determined to be 1.354×10^{-4}.

This study shows that occupational exposure to[232]Th radionuclide by ingestion should posesno threat to the health of workers. Guidelinesfor monitoring processes and methods for assessing[232]Th radionuclide intakes arising from occupational or public exposure are required.

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