Measurement and analysis of $^{233}$U from local thorium by using gamma spectrometry and DNCS methods

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Abstract. The measurement and analysis of $^{233}$U from irradiated local thorium sample by gamma spectrometry and fission-induced delayed neutron counting system (DNCS) methods have been done. The sample was a small high purity local ThO$_2$ produced from the extraction of monazite sand at our research center. The main goal of this experiment was to explore possibilities of $^{233}$U determination in the irradiated thorium for its future use in SAMOP reactor. Some ThO$_2$ samples of 0.1 gram were irradiated at the Kartini reactor at average neutron flux of $10^{12}$ n cm$^{-2}$s$^{-1}$ and cooled down for 55 days before counted by gamma spectrometry where $^{233}$U determined indirectly by gamma peak counting of $^{233}$Pa. The samples then re-irradiated to determine $^{233}$U by using DNCS method. The analysis result both by using gamma spectrometry and DNCS methods were $10.10 \pm 0.96 \mu g$ and $17.22 \pm 1.85 \mu g$ of $^{233}$U in average. Of the two gamma spectrometry and DNCS methods both provided results in somewhat relatively good agreement with the calculated amounts of $^{233}$U using ORIGEN2 computer code i.e. 14.3 $\mu g$. The detection limit of DNCS and the efficiency of detection system measured are $0.006 \mu g$ and $6.39 \pm 0.07\%$ respectively, and the efficiency of gamma spectrometry system is $17.8\%$.

Keywords: $^{233}$U, measurement, ThO$_2$, Kartini reactor, DNCS, SAMOP.

1. Introduction.

Thorium (Th) is a radioactive metal with atomic number of 90. Natural thorium contains one isotope, $^{232}$Th, which is an alpha-emitter with a half-life of 1.4 $10^{10}$ years. Although $^{232}$Th is a nonfissile isotope, it can be used as a nuclear reactor fuel through a breeding process i.e. neutron is capture by $^{232}$Th then breed to $^{233}$U as fissile material. Production energy of thorium is 20 million times the energy of coal and it can be used as an ideal source of energy [1].

Thorium-based fuel is usually composed in form of (Th-U)O$_2$ and (Th-Pu)O$_2$. The research carried out on thorium-based fuels indicates that these fuels can be considered as economic alternatives with improved physical properties and proliferation resistance issues. Thorium-based fuels offer some advantages over U-based fuels due to their high conversion factor capability in both thermal and fast neutron spectra. Moreover, their proliferation resistance characteristic makes them suitable alternatives for nuclear reactors [1,2]. Based on neutronic characteristic $^{233}$U bred from thorium is the best of the three nuclear fuels, $^{235}$U, $^{239}$Pu, and $^{233}$U and this for most neutron energies practically envisaged for power reactors, either thermal or epithermal. The reproduction factor ($\eta$) i.e. average number of fission neutrons produced for each thermal neutron absorbed in the fuel is higher to that of $^{235}$U or of $^{239}$Pu. This means that $^{233}$U will be a good fuel in any reactor type. In addition, some authors claim that the fission products which accumulate in a thorium-based reactor are less poisoning from neutronic point of view than those from a uranium-based one [2].
Thorium-based fuel can be used in several types of reactors, such as the Boiling Water Reactor, Pressurized Water Reactor, and Fast Reactor [3,4,5] as well as Pressurized Heavy Water Reactor, Molten Salt Reactor, and High Temperature Reactor [6,7]. One of the main problems in using thorium-based fuel is the so-called protactinium effect $^{233}$Pa, which can increase potential reactor criticality. Such a phenomenon is highly undesirable, causing reactor restart and operation control very challenging. This phenomenon is especially crucial for thermal breeders, in which the $^{233}$Pa(n,$\gamma$)$^{234}$Pa reaction with a rather high cross-section and short half-life ($t_{1/2} = 6.70$ h) takes place. Hence, $^{233}$Pa should be timely removed from the area of high neutron density to prevent losses of the fissile $^{235}$U [8]. Therefore, fast and sensitive analytical methods are needed for determination of $^{233}$Pa and $^{233}$U for further studies of the thorium-based fuel cycle, inventory and safeguard purposes, and for future utilization.

The determination of $^{233}$U is a much more demanding analytical task, several methods have been developed such as inductively coupled plasma atomic emission spectrometric, and radiometric i.e. accounting with argon gas flow proportional counter. In this work, two methods were employed for determination of $^{233}$Pa and $^{233}$U in neutron irradiated thorium. For the former radionuclide, gamma spectrometry was used, while for the latter radionuclide neutron activation analysis (NAA) with counting of delayed neutrons was applied. The results obtained were compared with data calculated with ORIGEN-2 software package.

The research aim is to investigate $^{233}$U content from irradiated local thorium processed in our research center, as part of a local thorium potential assessment program in cooperation with PT Timah [9]. The local thorium is extracted from monazite sand purified to form $^{9}$ThO$_2$. ThO$_2$ samples was irradiated by neutron in Kartini reactor irradiation facility and counted by using gamma spectrometry. Kartini reactor provided by several irradiation facilities operating at 100 kW and still in a good performance since ageing management applied to this reactor [10,11]. The samples were cooled down for a month then re-irradiated and counted by using delayed neutron counting system (DNCS) facility.

2. Material and method.

Interactions of fissionable nuclei with neutron may produce radioactive fission products and 2 or 3 prompt neutrons. Several these fission products may emit neutrons in achieving the stable state, these neutrons is called delayed neutron. These radioactive fission products, which have the capability to emit prompt neutrons. Several these fission products may emit neutrons in achieving the stable state, these groups vary somewhat depending on the fissile material in use. Table 1 lists the characteristics for the six precursor groups resulting from thermal fission of $^{233}$U, $^{235}$U and $^{232}$Th [6,12]. The fraction of all neutrons that are produced by each of these precursors is called the delayed neutron fraction for that precursor. The total fraction of all neutrons born as delayed neutrons is called the delayed neutron fraction (β). The fraction of delayed neutrons produced varies depending on the predominant fissile nuclide in use. The delayed neutron fractions (β) for the fissile nuclides of most interest are as follows; $^{233}$U (0.0026), $^{235}$U (0.0065), $^{238}$U (0.0148), and $^{239}$Pu (0.0021).

| Group | Precursor | Energy (MeV) | Precursor half-life t$_{1/2}$ (s) | Delayed neutron fraction $^{235}$U $^{233}$U $^{235}$Pu $^{233}$Pu | β (%) |
|-------|-----------|-------------|-----------------------------------|---------------------------------------------------------------|-------|
| 1     | $^{87}$Br, $^{142}$Cs | 0.25 | 55.72, 54.28, 55.0 | 0.021, 0.070, 0.0226 | $^{235}$U $^{233}$U $^{235}$Pu $^{233}$Pu |
| 2     | $^{131}$I, $^{88}$Br | 0.56 | 22.72, 23.04, 20.57 | 0.140, 0.0626, 0.0786 | | |
| 3     | $^{131}$I, $^{89}$Br, $^{93,94}$Rb | 0.43 | 6.22, 5.60, 5.00 | 0.126, 0.0444, 0.0658 | | |
| 4     | $^{131}$I, $^{94}$Kr, $^{143}$Xe | 0.62 | 2.3, 2.13, 2.13 | 0.252, 0.0685, 0.0730 | | |
| 5     | $^{140}$I, $^{145}$Cs | 0.42 | 0.61, 0.618, 0.615 | 0.074, 0.018, 0.0135 | | |
| 6     | (Br, Rb, As etc) | - | 0.23, 0.257, 0.277 | 0.027, 0.0093, 0.0087 | | |

Table 1. Data of delayed neutron from fissile materials [6,12].
$^{232}$Th is a good fertile material, because if it is irradiated by neutrons yields a new fissile nuclide $^{233}$U by two successive beta decays of $^{233}$Th following equation (1) and as depicted in Figure 1. As can be seen from Figure 1, $^{233}$Pa is formed by $\beta$ decay from $^{233}$Th and will form $^{233}$U thorough $\beta$ decay with $t_{1/2} = 27$ days. Whiles, $^{233}$Pa ($n,\gamma$) $^{234}$Pa reaction takes place with a cross-section $38.34 \pm 1.78$ barn for the 25.3 meV neutrons, with half-life $t_{1/2} = 6.70$ h [12,13]. $^{233}$Pa therefore, can be measured by using gamma ray spectrometry because this radionuclide emits gamma-lines with the main energies of 312.01 keV (36%), 300.18 keV (6.2%), 340.59 keV (4.2%), and U K-X-rays of 98.44 keV (16%) and 94.67 (10.2%) well measurable with semiconductor HPGe detectors. On the other hand, determination of $^{233}$U is a much more demanding analytical task [8].

\[
\begin{align*}
^{232}Th \rightarrow^{233}Th \rightarrow^{233}Pa \rightarrow^{233}U
\end{align*}
\]

Figure 1. Nuclear transmutations of $^{232}$Th by neutron irradiation [8]

In this work, two methods were employed for determination of $^{233}$Pa and $^{233}$U in neutron irradiated thorium. The isotope $^{233}$Pa which will decay to form $^{233}$U is determined by gamma spectrometry, while $^{233}$U is determined by DNCS. The results obtained were compared with data calculated by Origen-2 software package.

### 2.1 Gamma-spectrometry

Measurement of the $^{233}$Pa activity was carried out with an absolutely calibrated coaxial HPGe detector with relative efficiency of 17.8%, and FWHM resolution of 1.8 keV for the 1332.5 keV photons of $^{60}$Co, using Canberra Genie 2000 gamma-spectrometric system. A sample-to-detector distance was 75 cm. A mass of $^{233}$U formed during irradiation of the $^{232}$Th target and created after a decay time $t_d$ can be calculated as [8].

\[
t_{d}^{233}U = \left(\frac{233PaA}{233PaM} - \frac{233PaA}{233PaM} t_{d}^{-1} \right) \left( 1 - e^{-\lambda t_{d}} \right)
\]

where: $233PaA$ is activity of $^{233}$Pa at the end of irradiation, M is molar mass and $N_A$ is Avogadro’s constant. After the decay time of 55 days employed in this work, 20% of the $^{233}$Pa nuclei formed upon irradiation was transformed into $^{233}$U nuclei.

### 2.2 DNCS (delay neutron counting system)

Principle of delayed neutron counting system (DNCS) is a nuclear activation analysis method that is used to measure uranium and thorium in sample matrices without chemical processing. Neutron irradiation of thorium and uranium induces nuclear fission reactions yielding fission products that subsequently decay by delayed neutron emission. Most other naturally occurring elements undergo neutron capture reactions yielding radioisotopes which subsequently undergo beta/gamma decay.
Delayed neutrons from an irradiated sample can be selectively and quantitatively counted with practically no interference from beta/gamma emitters. Figure 2 shows a custom-built, automated DNCS facility integrates the sample loader, irradiation termini, transfer systems, and neutron counters with a computer that provides on-line experiment control and data handling.

The neutron irradiation tube located at F-ring of Kartini reactor core, from the computer control unit can be adjusted the irradiation time, and the necessary signals to the sample loader to load, blow in and blow out samples. Fast sample transport from neutron source (reactor core) to the neutron detector with transfer time ~ 3.3 seconds, distance between reactor core and the neutron detector ~ 55 m, sample speed ~ 16.7 m s\(^{-1}\). The neutron detector of DNCS is an assembly of 2 BF\(_3\) proportional counters (LND) connected to a pulse-height analyzer ORTEC and PC computer.

**Figure 2.** Schematic diagram of DNCS facility at Kartini reactor [9]

3. Results and Discussion

3.1 Gamma spectrometry analysis result

Five samples of ThO\(_2\) each 0.1 g of mass were irradiated for 100 hours at irradiation facility of Kartini reactor. When the reactor is shut down, the sample is taken and counted using a gamma spectrometry. One of the results of gamma spectrometry analysis showed \(^{233}\)Pa activity of 38090623.83 ± 88018.6 Bq or 1.0295 ± 0.003 mCi. The \(^{233}\)Pa element identified at 311.9 keV energy that has a probability of 33.70\% (the largest probability). The results of gamma energy of irradiated ThO\(_2\) sample are further shown in Table 2, Figure 3 and Figure 4. The \(^{233}\)Pa activities for irradiated ThO\(_2\) samples and its \(^{233}\)U content calculated by using equation (2) is presented in Table 3. The average \(^{233}\)U measured is 16.8043 ± 1.2019 in average.

| No | Gamma energy (keV) | Probability (%) |
|----|-------------------|-----------------|
| 1  | 75.28             | 1,150           |
| 2  | 86.61             | 1,790           |
| 3  | 271.54            | 0,840           |
| 4  | 300.11            | 5,800           |
| 5  | 311.9             | 33,700          |
| 6  | 340.47            | 3,880           |
| 7  | 375.40            | 0,590           |
| 8  | 390.50            | 1,290           |
| 9  | 415.75            | 1,590           |

**Table 2.** Gamma energy spectrum of \(^{233}\)Pa from irradiated ThO\(_2\)

**Figure 3.** Gamma energy spectrum of \(^{233}\)Pa
Figure 4. Gamma energy spectrum of $^{233}$Pa (linear scale)

Table 3. Average $^{233}$U content calculated by using equation (2)

| Sample code | $^{233}$Pa activity (Bq) | $^{233}$U mass (µg) |
|-------------|--------------------------|---------------------|
| Th1         | 11959513379              | 15.7908             |
| Th2         | 12779958845              | 16.8740             |
| Th3         | 1220729008               | 16.1179             |
| Th4         | 1222115273               | 16.1375             |
| Th5         | 14466842198              | 19.1013             |
| Average     |                          | 16.8043 ± 1.2019    |

3.2 DNCS result

Determination of $^{233}$U mass is based on the proportion between a nuclide amount and the number of detected delayed neutrons for two nuclides, i.e. $^{233}$U and $^{235}$U according to equation (3) as follows [8]:

$$ m^{^{233}} = \frac{I^{^{233}} \cdot m^{^{235}} \cdot \nu_d^{^{233}}}{I^{^{235}} \cdot \nu_d^{^{235}}} $$

where $m^{^{233}}$, $I^{^{233}}$, and $\nu_d^{^{233}}$ are mass of $^{233}$U, intensity (count/s), and number of delayed neutrons per one fission of $^{233}$U respectively, whiles $m^{^{235}}$, $I^{^{235}}$, and $\nu_d^{^{235}}$ are mass, intensity (count/s), and number of delayed neutrons per one fission of $^{235}$U respectively. The number of delayed neutrons per one fission of $^{233}$U and $^{235}$U ($\nu_d^{^{233}}$ and $\nu_d^{^{235}}$ ) are 0.00667 and 0.0167 respectively [10].

Five samples of irradiated ThO$_2$ (0.1 g each) after cooled down for 118 days and a standard depleted uranium sample, were irradiated for 120 s at irradiation facility of Kartini reactor with thermal neutron flux of 4.5x10$^{11}$ n/cm$^2$s. At the end of irradiation time the sample is pneumatically transferred to the detection system of DNCS for $^{233}$U measurement. The detection limit of DNCS and the efficiency of detection system measured are 0.006 µg and 6.39 ± 0.07% respectively. The $^{233}$U measured from the DNCS results are presented in Table 4.

Table 4. DNCS result for irradiated ThO$_2$ samples with average weight of 0.1 g

| ThO$_2$ sample | Intensity (cps) | $^{233}$U mass (µg) |
|---------------|----------------|---------------------|
| Th1           | 6.61           | 7.158984851         |
| Th2           | 16.49          | 19.00992918         |
| Th3           | 13.69          | 15.78204551         |
| Th4           | 16.59          | 19.12521074         |
| Th5           | 13.02          | 15.00965906         |
| Average       |                | 15.21716587         |
| STD-U         | 121.26         | $^{235}$U mass: 350 (µg) |
Theoretical calculations were performed with ORIGEN-2 computer code for ThO$_2$ samples irradiated for 100 hours as function of neutron flux, the result is presented at Figure 5. It is shown that for 0.1 g ThO$_2$ sample irradiated for 100 hours at neutron flux of $10^{12}$ n/cm$^2$s, will produce about $1.4 \times 10^5$ g $^{233}$U [9].

![Figure 5. Calculations of $^{233}$U production from ThO$_2$ samples irradiated for 100 hours as function of neutron flux performed by ORIGEN-2.](image)

The DNCS counting spectrum for blank sample capsule, standard $^{232}$Th (E-Merck), standard U-depleted (Reactor Experiment), ThO$_2$ sample, are shown in Figure 6 and Figure 7. It is clear from the figures that all have a similar spectrum profile, this mean that the ThO$_2$ sample has a high purity similar with the standard sample from Reactor Experiment and E-Merck.

![Figure 6. The DNCS counting spectrum for blank sample capsule (A) and standard $^{232}$Th E-Merck (B)](image)

![Figure 7. The DNCS counting spectrum for standard U-depleted sample (A) and ThO$_2$ sample (B)](image)
4. Conclusion.
The measurement and analysis of $^{233}$U from irradiated local thorium sample have been done. The analysis result both by using gamma spectrometry and DNC methods were 10.10 ± 0.96 µg and 17.22 ± 1.85 µg of $^{233}$U in average, whiles, the average calculated amounts of $^{233}$U using ORIGEN2 computer code is 14.3 µg. The detection limit of DNCS and the efficiency of detection system measured are 0.006 µg and 6.39 ± 0.07% respectively. A slightly different results between gamma spectrometry and DNC methods, the most probable reason is the insufficient knowledge of differential neutron spectrum in irradiation facility of the Kartini reactor used for determination of $^{233}$U nuclide by DNC.

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