LA-UR-16-23836
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Title: 238Pu02 Fuel and Dosimetry

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Intended for: Report

Issued: 2016-06-02

$^{238}PuO_2$ Fuel and Dosimetry

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June 1, 2016

Abstract

^{238}Pu is an ideal material for use as a heat source with its half-life of 87.7 years and copius α-particle emissions. ^{238}Pu radioisotope thermoelectric generators (RTGs) have found use for pacemakers, Apollo Space missions, Mars rovers, and Voyager spacecraft. In evaluating the dose to personnel and components near a ^{238}Pu-based RTG, a number of additional nuclides and their daughter products must be considered to get an accurate estimate for γ-dose and the amount of ^{17}O and ^{18}O for the neutron-dose must be considered. This paper looks at the contributing nuclides and their daughter products that add the most to the dose rates.

1 Introduction

^{238}Pu radioisotope thermoelectric generators (RTGs) have found use for pacemakers, NASA Missions (Voyager, Apollo, Mars rovers, Cassini-Hyugens, New Horizons), and other national security applications. Although reactor grade plutonium contains ^{238}Pu, using reactor grade plutonium as a source material requires costly isotopic separation techniques. The main method for production of ^{238}Pu is through the irradiation of ^{237}Np [5].

$$^{237}\mathrm{Np} \underset{2.144x10^6y}{\xrightarrow{(n,\gamma)}} {}^{238}\mathrm{Np} \xrightarrow[2.1d]{\beta} {}^{238}\mathrm{Pu}(t_{1/2} = 87.7y)$$

This results in materials that are $\approx$83% ^{238}Pu of the total plutonium content. Depending on the applications, different specifications have been adopted to minimize the dose to surrounding people or materials. One of the major contributors to dose was identified as ^{236}Pu. Unfortunately ^{236}Pu is also produced through two reactions with ^{237}Np in the reactors. Proper care can be taken in the production to reduce this contributor to a few ppm by appropriately shielding the ^{237}Np during irradiation. Complete removal has not been practical. It is the decay of ^{236}Pu into ^{232}U and its daughters into ^{208}Tl that produce a significant number of 238.6-, 583.2-, and 2614-keV γ-rays.

For the milliwatt generator (MWG) project [4], $^{238}PuO_2$ materials were used to fabricate heat sources for RTGs. The only requirements for these RTGs were the number of emitted neutrons/second/gram of plutonium. For medical and NASA applications, more stringent specifications are in place. Besides documentation for the MWG project, other reports looked into impact of ^{236}Pu and its daughters to Mixed Oxide Fuels production [8] and the dose in aged plutonium [3].

2 γ-ray Dose from $^{238}PuO_2$ Milliwatt Generator Fuels

A example of a standard fuel mixture starting off with ≈83% ^{238}Pu is given in Table 1. More detailed information on the ranges of fuel mixtures can be found in Latimer's progress report and previous progress reports on the milli-watt generators [4]. The specific activity is given for each of the nuclides in terms of curies per gram ([Ci/g]). The fourth column in Table 1 gives the weighted specific activity for the fuel based upon the plutonium and americium being the only radionuclides present at the initial times.

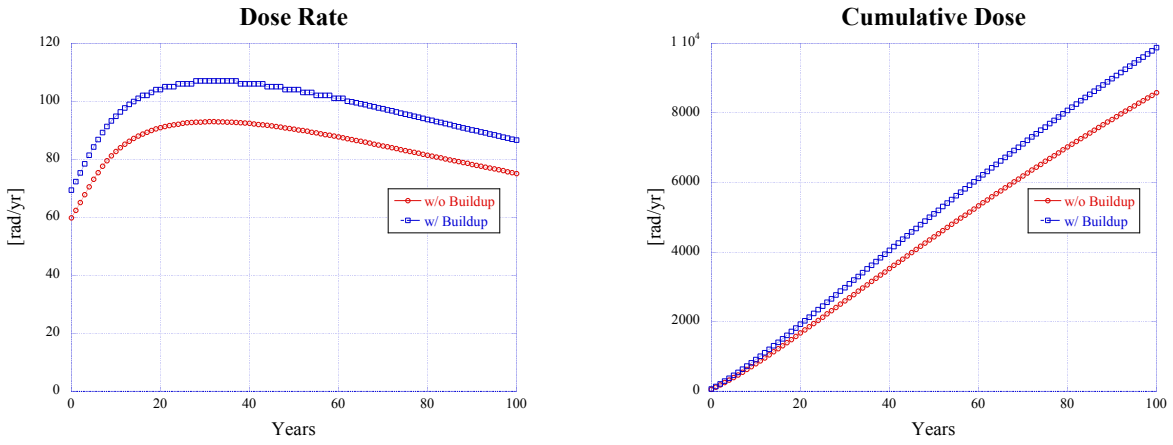
Table 1: Plutonium and Americium Contributions to Specific Activity in $^{238}PuO_2$ Fuel

Nuclide	**Specific Activity** [1, 9] **[Ci/g nuclide]**	**Weight Percent [%]**	**Fuel [Ci/g Pu]**
^{241}Am	3.42 x 10^{0}	0.0119	4.07 x 10^{-4}
^{236}Pu	5.29 x 10^{2}	0.0001	5.29 x 10^{-4}
^{238}Pu	1.71 x 10^{1}	83.56	1.43 x 10^{1}
^{239}Pu	6.19 x 10^{-2}	13.90	8.60 x 10^{-3}
^{240}Pu	2.27 x 10^{-1}	1.955	4.42 x 10^{-3}
^{241}Pu	1.03 x 10^{2}	0.455	4.70 x 10^{-1}
^{242}Pu	3.93 x 10^{-3}	0.128	5.03 x 10^{-6}

Consider a simple case whereby we have a 1-g sample of the fuel surrounded by 1-cm of stainless steel and we look at the dose rate to a point 10-cm away. The γ-ray dose rate ([rad/yr]) for this as a function of time is shown in Fig. 1a [1]. The difference between the w/ and w/o buildup takes into account buildup factors for γ-ray dose. If one had 10-g of fuel, the dose rate would be 10× larger. Similarly, one can estimate the cumulative dose [rad] for the same source, as shown in Fig. 1b. A breakdown of dose related to each of the initial plutonium and americium isotopes is given in Fig. 2. The line representing ^{241}Pu includes the decay of ^{241}Pu and its daughter products, including ^{241}Am. The line representing ^{241}Am is the contribution from the inital amount of ^{241}Am present. As one can see the ^{236}Pu, ^{238}Pu, and ^{241}Puplus their daughter products are the main contributors to the γ-ray dose.

Most of these MWG fuels were produced prior to 1990. If one were to take the fuel and remove the daughter products after 40 years, the resulting dose rate would be reduced, as shown in Fig. 3.

[1] Performed with Microshield ® Grove Software, http://radiationsoftware.com/microshield/



(a) (b)

Fig. 1: $^{238}PuO_2$ Fuel (a) Dose Rate and (b) Cumulative Dose with and without buildup as a function of year for 1-g of initial starting material

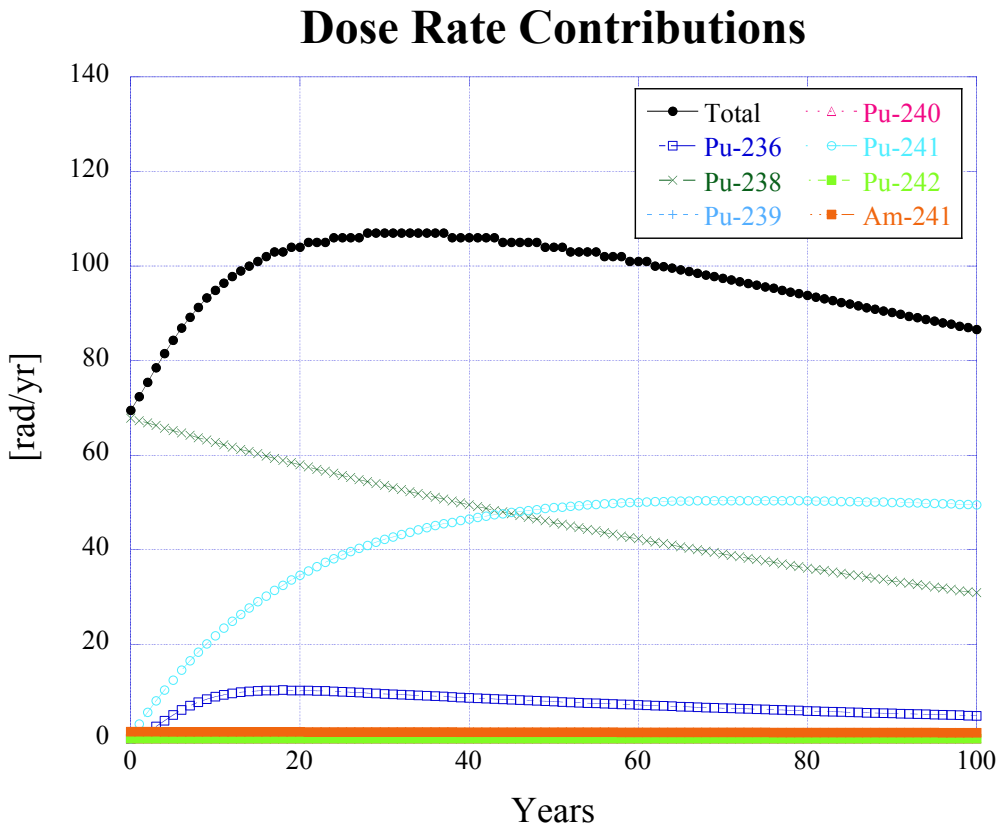


Fig. 2: Contributions of the plutonium isotopes and americium to the dose rate in 1-g of $^{238}PuO_2$ Fuel

By removal of the uranium and all daughter products at 40 years, the overall dose rate is reduced by ≈8 [rad/yr]. One has to be careful, however, as ≈23% of the plutonium has decayed away in that 40 years. One needs to correct for the disintegration of plutonium to generate the activity per gram of the cleaned fuel as is given in Table 2. Notice in Fig. 3, that there is a significant reduction between removal of the uranium only and the removal of ^{241}Am.

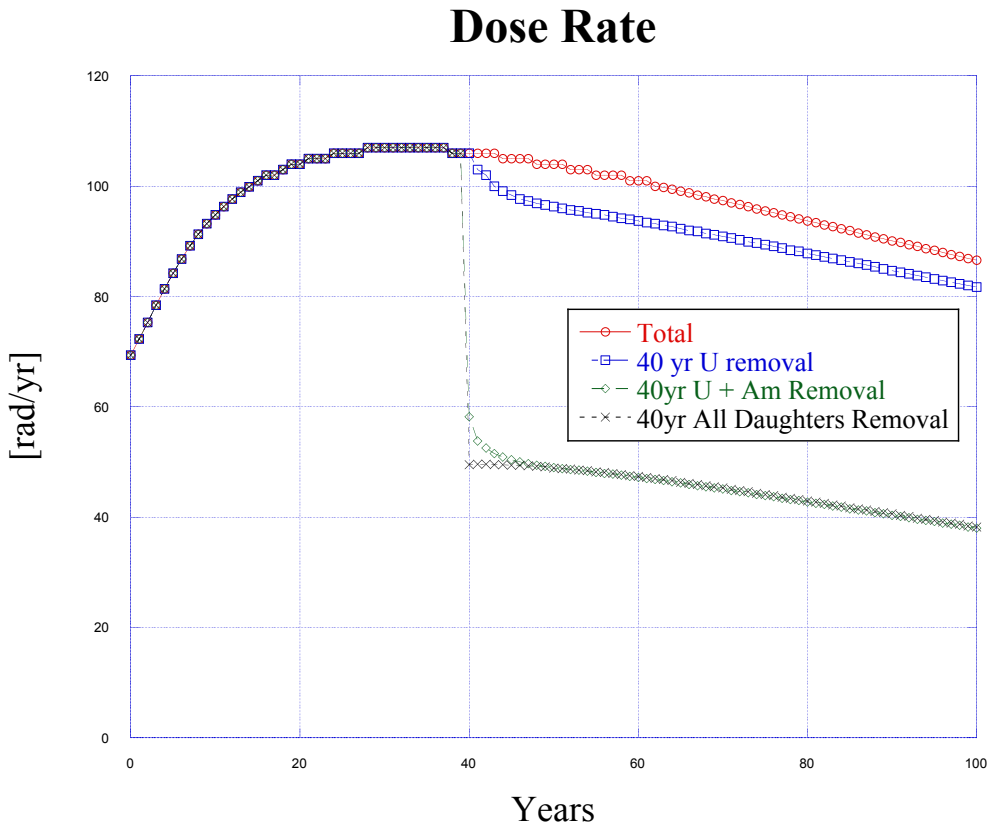


Fig. 3: Comparison of dose rate for $^{238}PuO_2$ Fuel with removal of uranium at 40 years and with removal of all daughter products at 40 years.

3 Neutron Dose from $^{238}PuO_2$ fuel Materials

The neutrons produced in $^{238}PuO_2$ come from four major sources: the spontaneous fission of ^{238}Pu and ^{240}Pu, and the (α,n) reaction on ^{17,18}O, and (α,n) on other impurities. The spontaneous fission rate of ^{238}Pu is 2.59 x 10^3 n/s/g and ^{240}Pu is 1.02 x 10^3 n/s/g [2]. The (α,n) contributions from elemental impurities and oxygen are given in Table 3. One of the standard practices is to expose the $^{238}PuO_2$ with oxygen isotopic exchange with ^{16}O in the form of $H_2{}^{16}O$ or $^{16}O_2$ [5].

Table 2: Plutonium and Americium Contributions to Specific Activity in Cleaned (i.e., daughters removed) 40 year old $^{238}PuO_2$ Fuel

Nuclide	**Specific Activity [Ci/g nuclide]**	**Weight Percent [%]**	**Fuel [Ci/g Pu]**
^{241}Am	3.04 x 10^{0}	0.5020	1.72 x 10^{-2}
^{236}Pu	5.30 x 10^{2}	$\approx$ 0.0000	4.12 x 10^{-8}
^{238}Pu	1.70 x 10^{1}	77.85	1.35 x 10^{1}
^{239}Pu	6.20 x 10^{-2}	18.04	1.12 x 10^{-2}
^{240}Pu	2.30 x 10^{-1}	1.80	5.73 x 10^{-3}
^{241}Pu	1.00 x 10^{2}	0.0862	8.91 x 10^{-2}
^{242}Pu	3.90 x 10^{-3}	0.128	6.54 x 10^{-6}

Table 3: Specific Neutron Yields from Light-element Impurities for 1 ppm impurity in ^{238}Pu [6]

Element	**Neutrons [n/s/g ^{238}Pu]**	**Element**	**Neutrons [n/s/g ^{238}Pu]**
Li	5.7	F	22
Be	162	Na	2.7
B	51	Al	1.2
C	0.2	Al	1.2
O	0.1	Si	0.2
^{17}O	0..62	P	< 0.03
^{18}O	6.25	S	< 0.03

The specification for medical-grade $^{238}PuO_2$ fuel [5] requires that

$$ppm^{18}\mathrm{O} + ppm^{17}\mathrm{O}/10 \leq 20ppm.$$

For comparison the specifications for the Mound Laboratory[2], the original producers of the MWGs, were ≤150 ppm ^{17}O and ≤ 50 ppm of ^{18}O.

4 Isotopic Determination of ^{238}Pu Fuels Measured at TA-55

The ^{238}Pu fuel for producing heat sources emit α-particles, β-particles, γ-rays, x-rays and neutrons. When estimating the dose rates and cumulative dose from the ^{238}Pu heat sources to personnel and surrounding materials, it is also necessary to take into account radiation emitted by the presence of other radioactive impurities within the fuels. As such, it is necessary to have a high quality radioactive nuclide characterization of these source materials.

The main source of additional γ radiation from ^{238}Pu fuel pellets arises from ^{236}Pu and its daughter products. The decay chain for ^{236}Pu is shown in the Fig. 4. The moderate ^{236}Pu content in the "ordinary" ^{238}Pu produced in the Savanna River Reactors was not considered critical for heat source applications. The typical ^{236}Pu content in "ordinary" Pu ranged from 0.8 to 1.2 ppm[5]. In the early 1970s for purposes of using ^{238}Pu in pacemakers, it was decided that permissible concentrations of ^{236}Pu and ^{232}U in freshly produced ^{238}Pu should not exceed concentrations that will produce a total γ dose over a 10-yr period greater than produced by 0.3 ppm of ^{236}Pu alone. Thus, concentrations of ^{232}U were tolerated in the ^{238}Pu if the corresponding ^{236}Pu concentration was less than 0.3 ppm. When considering ^{238}Pu fuel recycling, it was concluded that complete removal of ^{232}U and ^{228}Th was desirable as they both had short-lived γ emitting daughters such as ^{212}Pb, ^{212}Bi and ^{208}Tl. Out of these two, ^{232}U was considered to be the most important impurity, and for the purification cycle to be effective, 90% or more removal of ^{232}U was considered to be desirable [6].

Within the ^{238}Pu production process, the ^{236}Pu contamination mainly arises from two nuclear reactions

$$^{237}\mathrm{Np} \xrightarrow[2.144x10^6y]{(\gamma,n)} {}^{236}\mathrm{Np} \xrightarrow[22.4h]{\beta} {}^{236}\mathrm{Pu}(t_{1/2} = 2.858y)$$

$$^{237}\mathrm{Np} \xrightarrow[2.144x10^6y]{(n,2n)} {}^{236}\mathrm{Np} \xrightarrow[22.4h]{\beta} {}^{236}\mathrm{Pu}(t_{1/2} = 2.858y)$$

The threshold energy for both reactions is about 6.8 MeV. In production reactors, γ-rays of such high energy arise from neutron capture in the aluminum used for the reactor fuel cladding, housing tubes, target assemblies and other components. Some of the high energy γ-rays also come from Ni and Fe impurities in the aluminum alloy. The high energy neutrons come from fission

[2]Mound Laboratory in Miamisburg, Ohio, was a AEC and DOE sight closed in 2003.

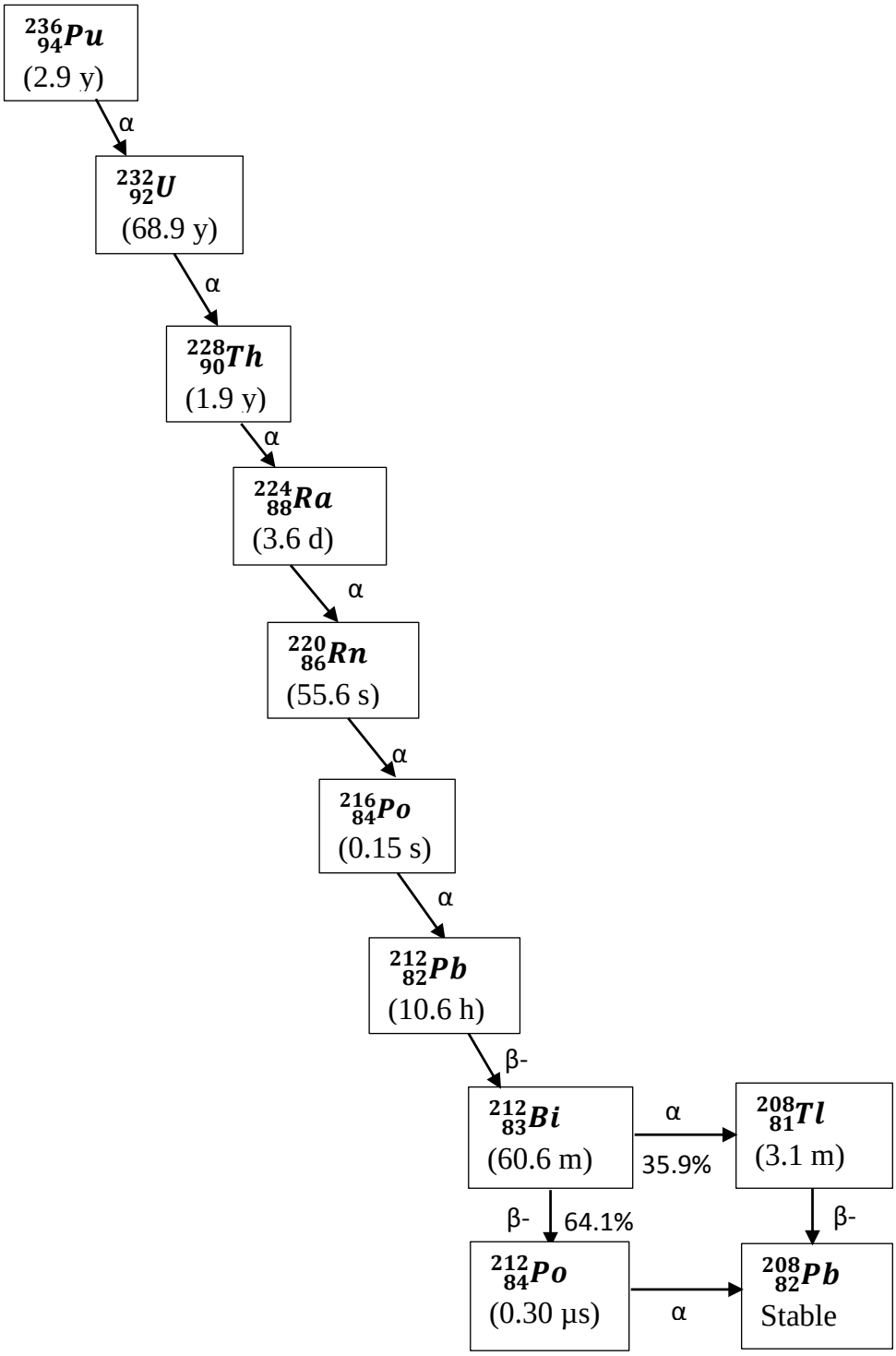


Fig. 4: ^{236}Pu Decay Scheme

reactions in the Pu isotopes and ^{238}Np. One way of reducing the ^{236}Pu contamination is eliminating these high energy neutrons and γ-rays from hitting the neptunium targets. One experiment[5] showed that ^{236}Pu contamination increased with longer irradiation time giving lower percent ^{238}Pu. In the same experiment aluminum matrix neptunium targets produced more ^{236}Pu than graphite-matrix-neptunium-targets, and locating graphite-matrix-neptunium-targets in the fringe of the reactor where neutron energy is relatively low resulted in reduced ^{236}Pu contamination.

The two other major contributors to radiation dose in the ^{238}Pu fuel pellets arises from ^{238}Pu and ^{241}Pu and its daughter products. The decay chains for both ^{238}Pu and ^{241}Pu are given in Fig. 5 and Fig. 6, respectively. Please note that some of the daughter products undergo β-decay, which is not taken into account in the γ-ray dose estimation. Other analyses for "extremely fresh" material, less than a year old, shows an enhancement to the dose because of thick target bremsstrahlung from the β-decays. This enhancement is being further investigated to determine the cause.

4.1 Fuel Measurements

Measurements were performed on three RTGs and loose source material at TA-55 [11]. These measurements included:

- Neutron and γ-ray dosimetry
- γ-ray measurement with an energy range from 0 - 4 MeV
- Calorimetry to determine the Pu mass from the heat output
- Neutron multiplicity analysis to determine the Pu mass, neutron leakage multiplication, and α-ratio (ratio of the number of (α,n) to the spontaneous fission neutrons)

The results from the standard radiological control technician dose measurements are given in Table 4. These samples are approximately 1/2 the mass of the expected system. A summary of the γ-ray data from standard nondestructive assay (NDA) is given in Table 5.

Table 4: Measured Dose Rates for CNS Fuels

Item	**Pu Mass**	**Neutron [mR/hr]**		**γ-ray [mR/hr]**		**Total [mR/hr]**	
	[g]	**Contact**	30-cm	**Contact**	**30-cm**	**Contact**	**30-cm**
0001	5.59	3.1	0.6	1.4	0.5	4.5	1.1
0002	4.19	2.4	0.5	0.6	0.4	3.0	0.9
0003	5.60	3.0	0.5	0.6	0.3	3.6	0.8

Both calorimetry and neutron multiplicity measurements and analyses were used to look at the mass of plutonium present and the number of neutrons being emitted. Based upon the calorimetry

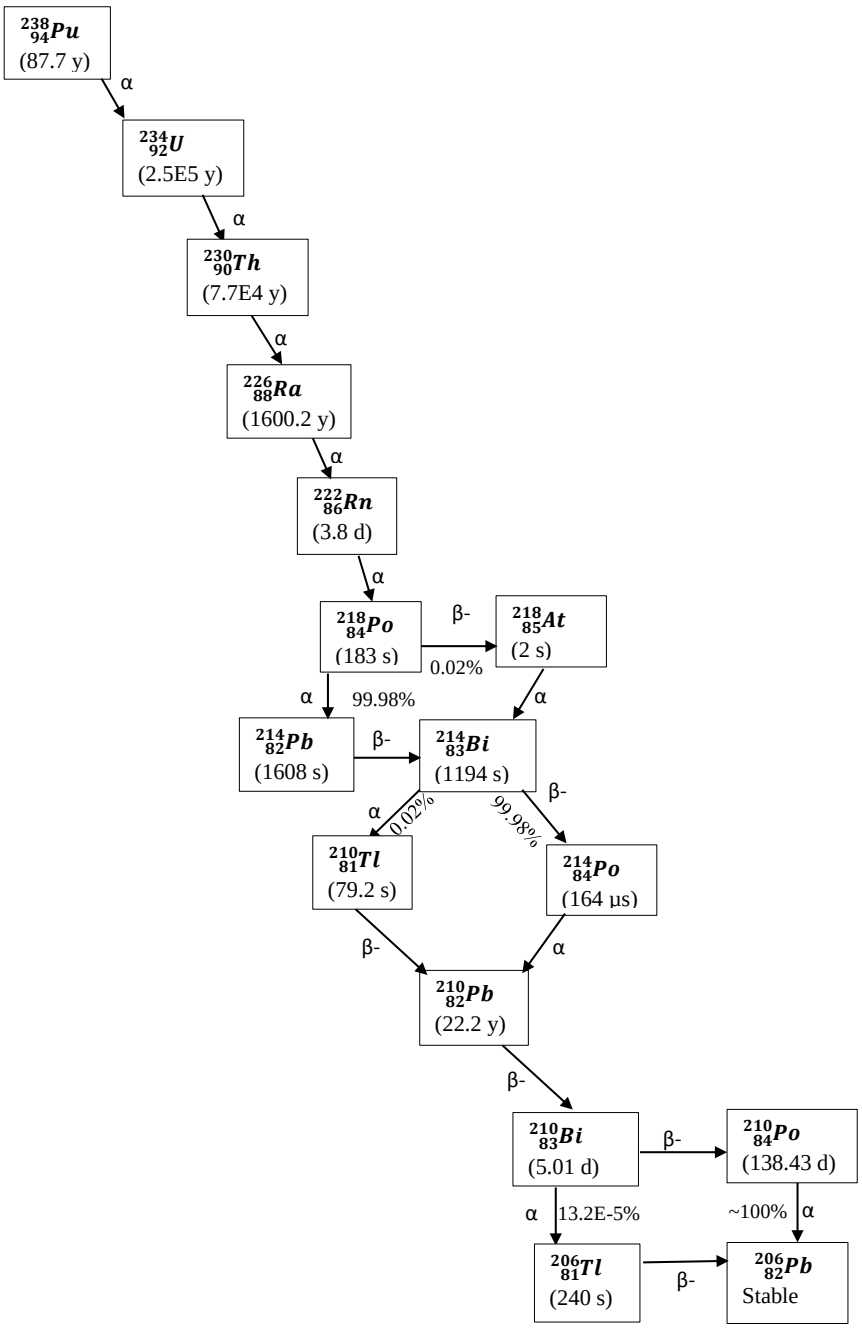


Fig. 5: ^{238}Pu Decay Scheme

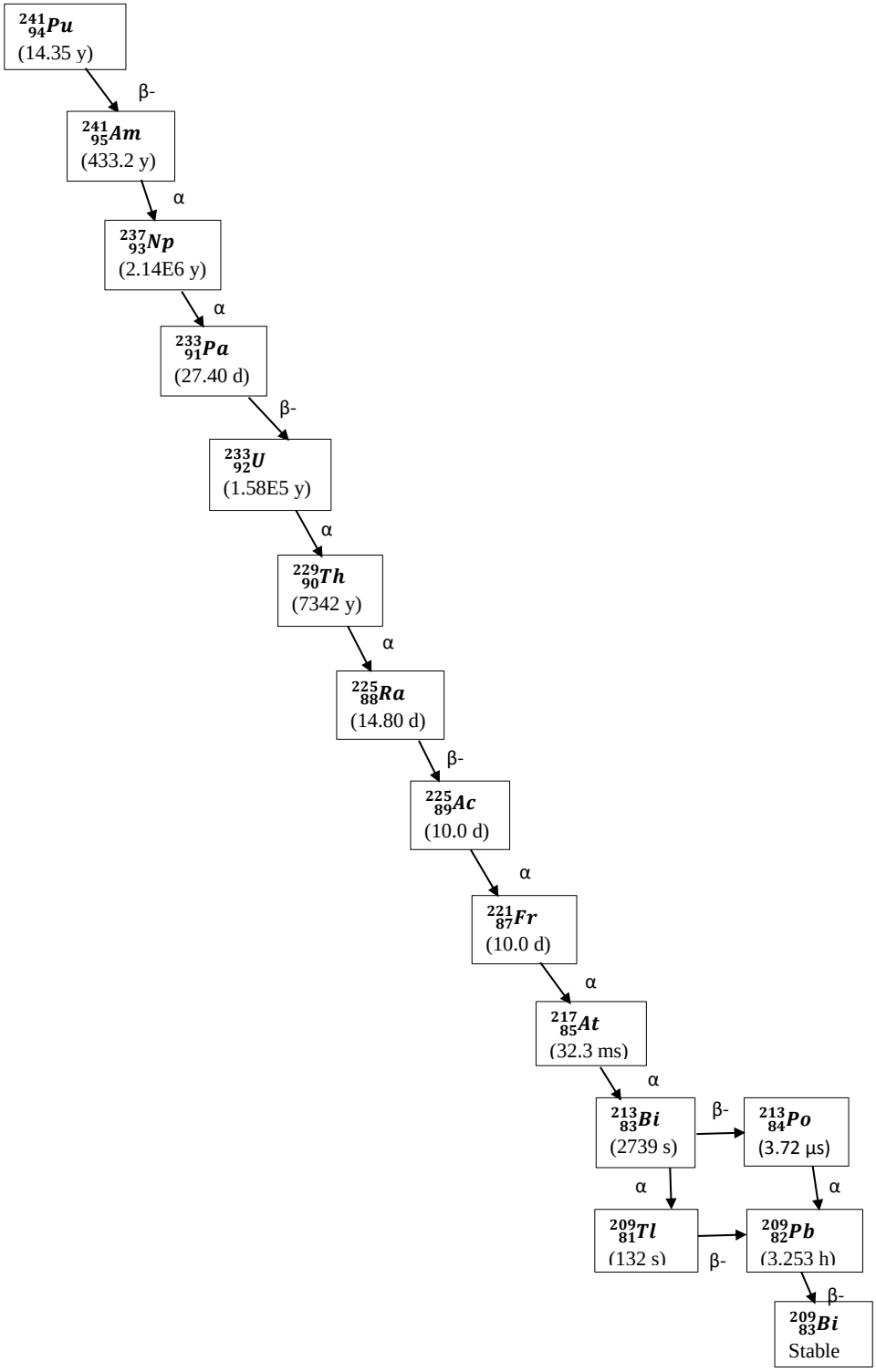


Fig. 6: ^{241}Pu Decay Scheme

Table 5: NDA γ-ray Pu Isotopics and ^{241}Am for CNS Fuels

Nuclide	Measured Value	Measurement Date
^{238}Pu [wt %]	75.60	March 18, 2015
^{239}Pu [wt %]	13.80	March 18, 2015
^{240}Pu [wt %]	1.90	March 18, 2015
^{241}Pu [wt %]	0.10	March 18, 2015
^{242}Pu [wt %]	0.08	March 18, 2015
^{241}Am [ppm]	6000	March 18, 2015

measurements, we get the measured wattage (Table 6) measured wattage, and when combined with isotopics, the Pu mass.

Table 6: Standard NDA Calorimetry Results for the CNS Fuels

Item Id	CNS-0001-2515	CNS-0002-2515	CNS-0003-2515
Measurement Date	September 2, 2015	September 3, 2015	September 2, 2015
Measured Watts	2.4065	1.8017	2.4073
P_{eff} (mW/g-Pu)	430.096	430.096	430.096
Pu Mass [g]	5.59	4.19	5.60

Utilizing the known mass of plutonium and the measured neutron output from the multiplicity counter, we were able to determine the numbers of neutrons per second per gram of plutonium. The neutron multiplicity counter has an efficiency for plutonium neutrons of 51.8%. Table 7 summarizes the results of the measurements for each sample.

Table 7: Neutron Output for CNS Fuels

Item Id	CNS-0001-2515	CNS-0002-2515	CNS-0003-2515
Measurement Date	September 1, 2015	September 1 , 2015	September 1, 2015
Measured Singles [n/s]	7,789.291 ± 3.072	5,855.654 ± 2.405	8,010.735 ± 2.808
Neutron Output [n/s/g-Pu]	2,690.025 ± 1.061	2,697.936 ± 1.108	2,761.561 ± 0.968

4.2 γ-ray Data Analysis for Impurities

FRAM [10] is a software program that calculates the isotopic ratios of plutonium, uranium, and others. It analyzes spectra acquired with high purity germanium (HPGe) γ-ray detectors. For the case of heat-source plutonium, FRAM can be utilized to determine ^{238}Pu/^{239}Pu, ^{238}Pu/^{240}Pu, ^{238}Pu/^{241}Pu, as well as ^{241}Am/plutonium, ^{237}Np/plutonium, ^{232}U/plutonium and others. FRAM was used to analyze the data collected.

Because FRAM is a self-calibrating program, the user only supplies the unknown spectrum to the software. The user chooses or creates a parameter set and clicks the 'Analyze' button. The software produces a table with the various isotopic ratios. The uncertainty of the isotopic ratios can be lowered by acquiring the spectra for more time and, to some extent, by counting with reduced source-detector distance. One has to be careful when setting up the detector to make sure that the dead time is not too high, as this can change the shape of the peaks and make the analysis more difficult. Limited experience with the available data acquisition system suggests that dead times of 40% to 50% can be analyzed with good results. Except for a very long 20 hour data accumulation, the spectra supplied have insufficient statistics to make the ^{240}Pu signal visible, so FRAM either reports zero for this isotope, or a virtually meaningless number with very large Relative Standard Deviation, RSD.

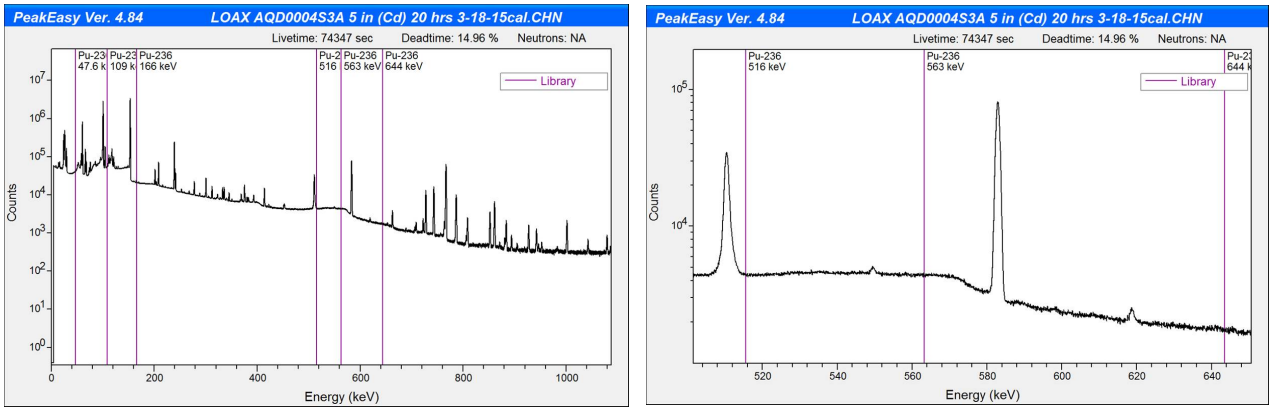
Given the relatively weak emissions from ^{236}Pu, coupled with the initial ppm-level concentration, and its short half-life, there is virtually never a ^{236}Pu signal present in aged ^{238}Pu heat source γ-ray spectra we have. The best one can do in these cases is set up FRAM to estimate the ^{232}U content, which can be used to determine over 90% of current and future dose contribution from the ^{236}Pu when the plutonium is sufficiently aged, approximately 10 years. Table 8 shows the results of our analysis using FRAM.

Table 8: Results of FRAM analysis for the three measured items.

Item Numbers	**^{238}Pu (mass %)**	**^{239}Pu (mass %)**	**^{240}Pu (mass %)**	**^{241}Pu (mass %)**	**^{232}U (ppm)**	**^{241}Am (mass %)**
0001	77.8 ± 4.7	22.0 ± 1.3	< 6.0	0.16 ± 0.02	0.26 ± 7.8%	0.71 ± 0.05
0002	77.6 ± 4.7	22.2 ± 1.4	< 6.1	0.14 ± 0.02	0.26 ± 7.9%	0.74 ± 0.05
0002 recount	78.2 ± 4.6	21.7 ±1.3	< 5.9	0.16 ± 0.03	0.22 ± 7.7%	0.71 ± 0.05
0003	78.0 ± 4.7	21.9 ± 1.3	< 6.0	0.15 ± 0.02	0.26 ± 7.7%	0.72 ± 0.05
Powder	75.4 ± 0.2	19.8 ± 0.1	3.9 ± 0.2	0.12 ± 0.00	0.36 ± 1.2%	0.69 ± 0.01

So far in the samples we measured and analyzed, we see less than 0.4 ppm of ^{232}U in our samples, which means that when these sources were initially produced the ^{236}Pu content was higher than 0.4 ppm of ^{236}Pu. The samples exceeded the 0.3 ppm of ^{236}Pu, which was the requirement for pacemaker power sources. The powder sample listed in Table 8 was taken for a live time of 74347 s (20 hour accumulation) with a Cd attenuator. We were able to see the ^{240}Pu signature with this extended run. Based upon these measured samples, we were not able to observe any ^{236}Pu in the data, which matches what we would expect based upon half-life. Fig. 7 provides both the full spectrum (7a) and the 500-650 keV expanded spectrum (7b). Since the Cd attenuator was used, the strongest ^{236}Pu line at 47-keV would not be observed. If one looks at the higher energy lines in Fig. 7b, there is no evidence of any structure, and no evidence of ^{236}Pu. The daughter products, however, are present.

Our results are consistent with previous work on γ-ray isotopic analysis using FRAM [7].



(a) (b)

Fig. 7: Spectra from $^{238}PuO_2$ Fuel Powder (a) Full spectrum and (b) 500 - 650 KeV expanded spectrum with Cd absorber

5 Summary and Conclusions

We have taken a look at ^{238}Pu fuel as a simple point source surrounded by 1-cm of iron shielding to investigate the relative contributions to dose. The γ-ray dose rate for ^{238}Pu fuel is initially driven by the ^{238}Pu decay and by the ^{236}Pu if not kept to less than a few ppm . After approximately 40 years the main dose contributor is a combination of the decay of ^{238}Pu and ^{241}Pu. If aged fuel were to be reused, after 40 years, and the ^{232}U and ^{234}U from ^{236}Pu and ^{238}Pu decay, respectively, were removed, a reduction in dose can be achieved. After 40 years, dose resulting from ^{241}Am produced from the decay of ^{241}Pu is the next major contributor to dose, and begins to exceed the contributions from ^{238}Pu and its daughters after $\approx$45 years for the example shown in this paper. Also note that the ^{238}Pu weight fraction would be $\approx$79% from the work presented here. Based upon our measurements and other measurements [7], these older fuels do not appear to have a detectable amount of ^{236}Pu. One could, however, use the ^{228}Th quantity to back-calculate the amount of ^{236}Pu mass fraction at the date of precipitation. The addition of freshly produced fuel or fuels from feedstock that are vastly different from those presented here, such as larger quantities of ^{236}Pu or ^{241}Pu will change the relative contributions and potentially increase dose. These calculations do not include the thick-target bremsstrahlung that occurs due to beta decay.

References

[1] J. S. Coursey, D. J. Schwab, J. J. Tsai, and R. A. Dragoset. Atomic weights and isotopic compositions with relative atomic masses, September 2015.

[2] N. Ensslin, W. C. Harker, M. S. Krick, D. G. Langner, M. M. Pickrell, and J. E. Stewart. "Application Guide to Neutron Multiplicity Counting". Manual LA-13422-M, Los Alamos National Laboratory, November 1998.

[3] D. E. Kornreich. "Analysis of the Dose from ^{236}Pu Progeny in Aged Plutonium". Technical Report LA-UR-12-27084, Los Alamos National Laboratory, December 2012.

[4] T. Latimer, T. George, C. Frantz, R. Matthews, and G. Rinehart. "Milliwatt Generator Project: April 1988 - September 1996". Progress Report LA-13528-PR, Los Alamos National Laboratory, July 1997.

[5] W. Lindsey, P. Roggenkamp, and W. Woods. "Production of ^{238}Pu with Minimum ^{236}Pu Contamination". *Nuclear Technology*, 13:78–82, January 1972.

[6] L. Mullins. "Preparation and Development of Medical-Grade Plutonium-238 Fuels, July 1, 1967 - June 30, 1971". Technical Report LA-4940, Los Alamos Scientific Laboratory, Octeber 1972.

[7] S. C. Myers, D. R. Porterfield, N. R. Carver, and R. K. J. anad L. A. Foster. "Gamma Ray Isotopic Analysis of Heat Source Plutonium (^{238}Pu) Using the FRAM Isotopic Code ". Technical Report LA-UR-15-22187, Los Alamos National Laboratory, March 2015.

[8] T. Sampson and T. Cremers. "The Concentration of ^{236}Pu Daughters in Plutonium for Application to MOX production from Plutonium from dismantled US Nuclear Weapons". Manuscript LA-13672-MS, Los Alamos National Laboratory, May 2001.

[9] J. K. Tuli. Nuclear wallet cards, October 2011.

[10] D. T. Vo. "Fixed energy, Response function Analysis with Multiple efficiences (FRAM) Tutorial". Technical Report LA-UR-15-26888, Los Alamos National Laboratory, September 2015.

[11] T. R. Wenz. "Measurement Report for CNS-0001-2515, CNS-0002-2515, CNS-0003-2515". Type, Los Alamos National Laboratory, September 2015.