PNNL-24355

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December 2014

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Abstract

We report on a technique to detect and quantify the amount of ^{240}Pu in a large tank used to store nuclear waste from plutonium production at the Hanford nuclear site. While the contents of this waste tank are known from previous grab sample measurements, our technique could allow for determination of the amount of ^{240}Pu in the tank without costly sample retrieval and analysis of this highly radioactive material. This technique makes an assumption, which was confirmed, that ^{240}Pu dominates the spontaneous fissions occurring in the tank.

Contents

1.0 Introduction

The detection and quantification of ^{240}Pu or other transuranic materials in inaccessible locations, such as underground waste cribs [Reference] or in highly radioactive environments would normally require collection of the sample, followed by radiochemistry to remove interfering isotopes and/or other radiometric technique (e.g., mass spectroscopy or radiation counting). We have explored a technique that allows for the indirect detection and possible quantification of ^{240}Pu using a straightforward method of ultra-sensitive detection of radioactive xenon gas which has been previously developed for other applications. We exploit that fact that ^{240}Pu has a relatively high spontaneous fission rate, producing Xe gas isotopes that have a high likelihood of escaping the immediate surroundings of the Pu. In the case investigated and reported on in this paper, we measure the short-lived radioactive isotopes of xenon which exhibit high mobility and may be sampled and measured using techniques normally used for the detection of nuclear explosions.

2.0 Production of fission gases by spontaneous fission in the headspace of a waste tank

Plutonium-240 decays nearly 100% of the time via α-emission to ^{236}U, though a small percentage of the decays (5.7×10^{-6}%) are via spontaneous fission. An effective spontaneous fission half-life, τ_{SF}, can be defined as the observed half-life divided by the branching ratio (BR) for spontaneous fission:

$$\tau_{SF} = \frac{\tau_{½}}{BR}. \quad [1]$$

The effective spontaneous fission half-life for ^{240}Pu is 6,560 yrs / (5×10^{-8}) = 1.34×10^{11} years. Table 1 below shows the spontaneous fission half-life and spontaneous fission yield for several transuranic isotopes including ^{240}Pu. One can easily see from the table that even isotopes of Pu (and U) have a much higher spontaneous fission rate than do the odd isotopes.

Table 2-1 Table of spontaneous fission half-lives and yields of selected isotopes

Isotope	Spontaneous Fission Half life (years)	Spontaneous Fission Fraction
^{252}Cf	85.5	0.03
^{244}Cm	1.35×10^{7}	1.3×10^{-6}
^{238}Pu	4.77×10^{10}	1.8×10^{-9}
^{239}Pu	5.48×10^{15}	4.4×10^{-12}
^{240}Pu	1.34×10^{11}	5.0×10^{-8}
^{242}Pu	6.84×10^{10}	5.5×10^{-6}
^{235}U	3.5×10^{17}	2.0×10^{-9}
^{238}U	8.2×10^{15}	5.5×10^{-7}

In spontaneous fission, the ^{240}Pu nucleus breaks apart into pieces that follow a mass distribution not too dissimilar to that of neutron-induced fission. The isotopes of xenon are among the higher yield mass fragments produced in this process. Table 2 shows some of the characteristics of the radioxenons produced in fission that are the subject of this paper.

Table 2-2 Characteristics of the xenon isotopes used in this study

Isotope	Half-life (d)	Decay Constant (s^{-1})	Cumulative Spontaneous Fission Yield (%)
^{131m}Xe	11.9	6.74×10^{-7}	0.047
^{133}Xe	5.2	1.53×10^{-6}	8.35 (Lestone)
^{133m}Xe	2.2	3.66×10^{-6}	0.19
^{135}Xe	0.38	2.11×10^{-5}	7.23

3.0 Technique to measure ^{240}Pu mass in a waste tank

Since spontaneous fission will create all of the xenon isotopes, by simultaneous measurements of several xenon isotopes, we can both determine the residence time of xenon isotopes in the waste form and also calculate the inventory of ^{240}Pu in the tank through the simple application of Bateman's equations. This approach assumes the Xe isotopes and ^{240}Pu are in secular equilibrium, which should be true unless there was a recent venting (within a few weeks of the sample collection) of the tank. Since the waste tank is a complex environment, however, we expected that some of the radioxenons may be held up in the matrix of the waste. While there is no guarantee that xenon produced in the tank waste would ever make it into headspace gas, it is possible to calculate an effective residence (hold-up) time for xenon using simultaneous measurements of the radioxenon fission gases that have different half-lives, ^{131m}Xe, ^{133}Xe, ^{133m}Xe, and ^{135}Xe. The spontaneous fission yields for each of the Xe isotopes determine the relative isotopic ratios when the Xe is born and the respective half-lives of the Xe isotopes determine how the ratios change with hold-up time. Therefore, a measure of the Xe isotopic ratio provides a means to determine the effective hold-up time. With a measure of the Xe gas concentration and a calculation of the Xe hold-up time it is possible to make an estimate of the quantity of ^{240}Pu.

Figure 1 shows a schematic illustration of the scheme we used for the sample collection from the headspace of the TX-118 tank. This particular tank was chosen based on an evaluation of historical data for underground storage tanks. Modeling was performed based on the type of waste present, its characterization and composition knowledge. Parameters such as access to tank head space and tank ventilation were also taken into consideration. A 1-inch polypropylene braided hose was fed through a 3-inch diameter sight glass of the tank level measurement equipment. The hose was inserted into opening of the hole to a depth of ~30 feet (as measured from the sight glass height). The opening was then sealed with tape and a plastic glove bag was placed sealed around the sight glass/hose. The sight glass is located on a riser approximately four feet above ground surface.

Two Whatman 0.7 μm microfiber glass filters were placed in line, as well as a ~12-inch length, 6-inch diameter Hi-Q, nuclear grade carbon trap. Following the carbon trap, ~100 feet of 2 inch

diameter corrugated hose was connected to a air compressor that compressed the headspace gas into six high pressure (4500 psi) cylinders. For this application, only two cylinders filled to 3900 psi were needed to supply the needed sample volume. During the sample collection, fill pressure was monitored every 20 minutes at a rate of ~500 psi every 20 minutes (~150 liters per minute) and the condensate collected in the compressor was removed. Each day the filters were counted and they showed a decrease in activity, which was attributed to radon daughters.

Initial measurements were performed by the injection of the headspace gas in compressed bottles which were transported to a remotely located SAUNA-II automated radioxenon measurement system. The SAUNA-II system is designed to measures xenon isotopes to concentrations well below 0.001 Bq/m^3. More information on the process for separating xenon from air samples and how the measurements occur is included in several references (Refs). Because the SAUNA relies on the total amount of xenon in the sample to calculate an effective volume sampled by the instrument, effects for stable xenon generation in the tank was calculated but found to be an insignificant effect (<<1%). An additional set of measurements were made using a similar laboratory-based beta-gamma based radioxenon measurement system (Reference) to validate the SAUNA-II measurements by using xenon gas samples archived by the SAUNA-II system. The second set of measurements was critical since the initial levels of ^{133}Xe measured in the first samples interfered with the ^{131m}Xe, making that isotope fall below detection limits. After an additional one month decay period after the initial measurement, the ^{131m}Xe observable above the ^{133}Xe signal. Figures 2(a) and (b) shows plots of one of the nuclear spectra obtained in this work, that clearly shows (a) the characteristic x- and gamma rays from ^{133}Xe, and (b) the conversion electron from ^{131m}Xe underneath the ^{133}Xe beta continuum.

Due to radiological safety concerns, the sample was taken off-site for approximately 5 days, so 2.2-day half-life ^{133m}Xe and the 9.1-hr half-life ^{135}Xe were expected to fall below detection limits. Therefore, in our measurements, we only measured two xenon isotopes ^{131m}Xe and ^{133}Xe. The measured values of ^{131m}Xe and ^{133}Xe decay corrected to sample collection time were 0.0097 and 2.68 Bq/m^3, respectively.

4.0 Simulation of the effect of passive venting

Single-shelled tanks at the Hanford site are usually vented to keep explosive gases below flammability limits. [Reference] Tanks can either be actively or passively vented, the latter is driven by barometric fluctuations, wind currents passing by openings in the tank and other effects. Since passive venting flows can be as high as 0.012 m^3/s (25 ft^3/min) [Reference] we have modeled the size of this effect with a model that assumes a constant flow, *F*, into and out of the TX-118 tank with a headspace volume of *V* (see Figure 3).

The governing equations for the accumulation of xenon isotopes inside a tank headspace from ^{240}Pu spontaneous fission are developed below. We will also assume that there is an average holdup time of t_H for fission product gases to migrate out of the waste into the headspace. Therefore, for times less than t_H, the only loss term is radioactive decay.

$$(1a) \quad \frac{dN_p}{dt} = -\lambda_p N_p$$

$$(1b) \quad \frac{dN_x}{dt} = f_x \lambda_P N_p - \lambda_x N_x \; for \; 0 < t < t_H$$

The solution to these equations is:

$$(2)\quad N_x(t) = \frac{f_x \lambda_P N_P^0}{\lambda_x - \lambda_P}\left(e^{-\lambda_p t} - e^{-\lambda_x t}\right) for\ 0 < t < t_H$$

After the gas reaches the headspace, venting from to the environment results in another loss term. The venting rate, **F** m^3/sec, and the headspace volume, **V** m^3, are assumed to be known. The source of xenon from the waste into the headspace, S_H, is the derivative of equation (2) evaluated at time t_H.

$$(3)\quad S_H = \frac{dN_x}{dt}|_{t_H} = \frac{f_x \lambda_P N_P^0}{\lambda_x - \lambda_P}\left(\lambda_x e^{-\lambda_x t_H} - \lambda_P e^{-\lambda_P t_H}\right)$$

We can now use equation (3) up time as the source term for gas in the headspace. Note that this approach neglects ^{240}Pu decay after the holdup time. This does not significantly affect the solution for realistic times.

The governing equation for the gas in the headspace is then:

$$(4)\quad \frac{dN_x^H}{dt} = S_H - \lambda_x N_x - \frac{F}{V}N_x\ for\ 0 < t < \infty\ where$$

The solution is:

$$(5)\quad N_x^H(t) = \frac{f_x \lambda_P N_P^0}{\lambda_x - \lambda_P}\left(\lambda_x e^{-\lambda_x t_H} - \lambda_P e^{-\lambda_P t_H}\right)\left(\frac{1 - e^{-\lambda_x^T t}}{\lambda_x^T}\right)$$

$$Here\ f_x = \left(\frac{SF}{decay}\right) * (SF\ yield\ for\ \text{x})$$

$$N_P^0 = Number\ of\ Pu240\ atoms\ at\ time = 0$$

$$\lambda_P = Pu240\ decay\ constant$$

$$\lambda_x = decay\ constant\ for\ nuclide\ \text{x}$$

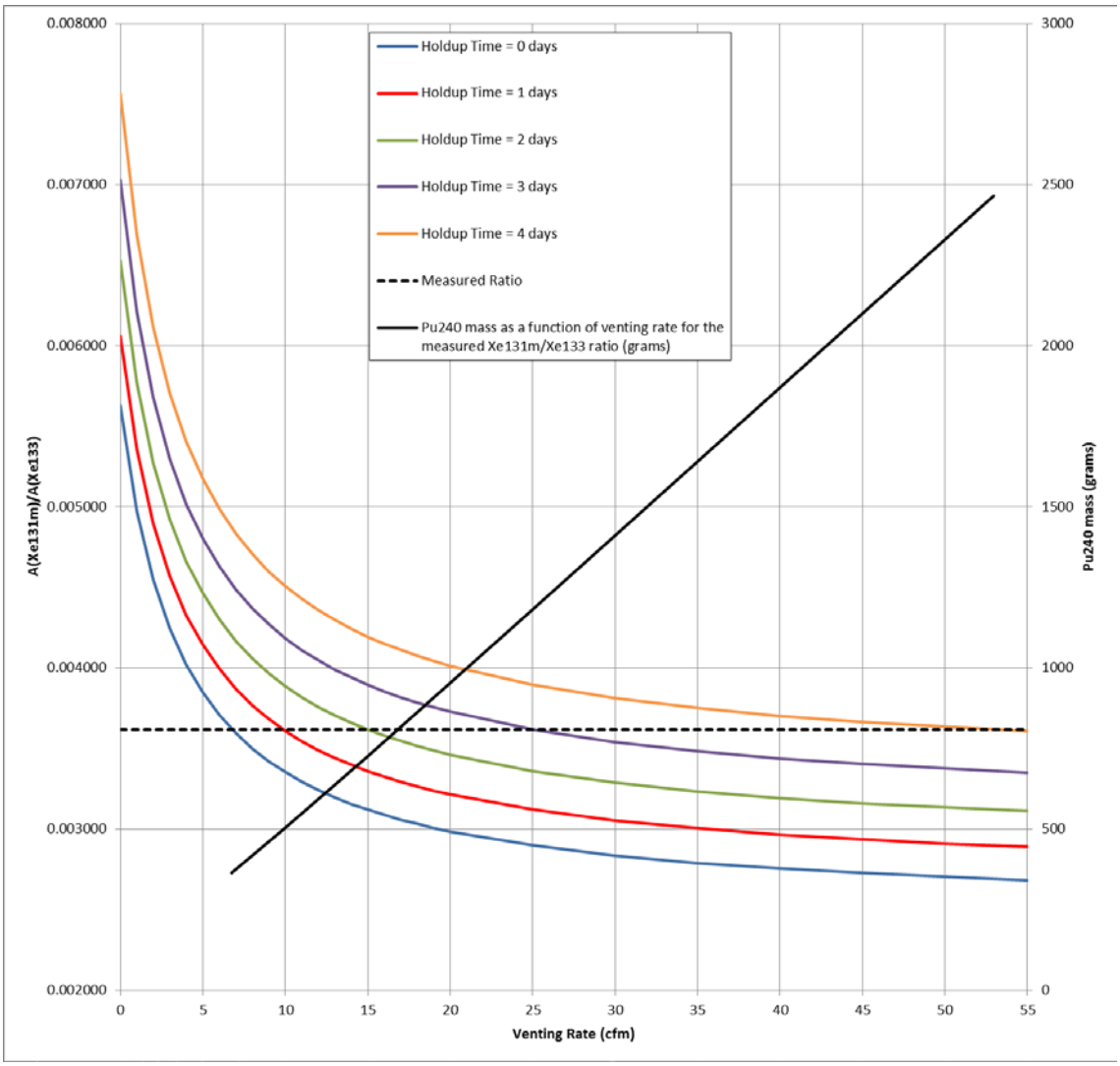
$$\lambda_x^T = \lambda_x + \frac{F}{V} = the\ total\ decay\ constant\ for\ nuclide\ x$$

If we assume no Pu^{240} decay, for long times, we obtain:

$$(6)\quad N_x^H(t \gg 0) = \frac{f_x \lambda_P N_P^0}{\lambda_x^T} e^{-\lambda_x t_H}$$

Previous work on Hanford tanks has shown that passive venting of the tanks can reach $50ft^3$/m, though most tanks have lower rates. For tank TX-118, no data exists for the passive flow from the tank during the period leading up to our collection.

Since only two xenon isotopes could be measured, and there are three unknowns (the ^{240}Pu mass, the holdup time and the venting rate), we can only provide a range of possible ^{240}Pu masses. In this case, we will use the activity ratio of ^{131m}Xe/^{133}Xe as a function of both holdup time and venting rate – this eliminates the ^{240}Pu mass. Then, a set of self-consistent holdup times and venting rates can be determined as shown in the figure below.



^{131m}Xe/^{133}Xe Activity Ratio as a Function of Venting Rate

In the above Figure, the equilibrium activity ratio is plotted as a function of venting rate for a variety of assumed holdup times. The measured ratio of 0.0036 is also plotted as a dashed line. The locations where this line intercepts the holdup time curves corresponds to the correct venting rate. The solid black line is the ^{240}Pu mass (read on the right hand side axis) that is consistent with the measured ratio, holdup time and venting rate with the following formula:

$$(6) \quad N_p^0 = \frac{\lambda_x^T N_x^{Measured}}{f_x \lambda_P e^{-\lambda_x t_H}}$$

The table below shows the results for several possible holdup times.

Table – TX-118 ^{240}Pu mass as a function of holdup time and venting rate

Holdup time (days)	**F (cfm)**	**^{240}Pu (grams)**
0	6.8	360
1	9.9	500
2	15	730
3	25	1200
4	53	2500

Since the maximum venting rate observed in Hanford waste tanks is bounded by about 50cfm, these results indicate a possible range of ^{240}Pu mass in tank TX-118 of 0.36 to 2.5kg. The published estimate of the actual inventory is $3.4\ ^{+3.4}_{-1.7}$ kg, which is quite reasonable agreement given the complex nature of the tank, measurement uncertainties and the fact that only two xenon isotopes could be measured.

5.0 Possible sources of uncertainty

Tank TX-118 is known to contain numerous transuranic isotopes including ^{240}Pu, ^{244}Cm and others. Other transuranic isotopes could potentially affect our results, since there is approximately 1.9 Ci (corrected to September 2013) of ^{244}Cm ($\tau_{½}$=18 yrs) was present in the tank during sampling. Referring to table 2, we can estimate that approximately 5% of the ^{133}Xe detected from the tank headspace was probably due to the spontaneous fissioning of ^{244}Cm, assuming that the distribution of Cm and Pu is approximately the same and the branching ratio of ^{244}Cm to ^{133}Xe is 5.7% (Reference) versus ~7% for ^{240}Pu. There is also a non-zero, but small neutron flux in the tank that is attributable to (α, *n*) reactions on light elements and a small amount from spontaneous fission of the transuranics. The estimated neutron flux in the tank is on the order of ~1 *n*/cm^2/sec (Reeder reference), and therefore we believe that the contribution to neutron-induced fission of ^{239}Pu and other elements is small.

There are several possible factors that could lead to an underestimate of ^{240}Pu, including the ^{133}Xe in the tank could be diluted in another way, perhaps with a much higher ventilation rate than we expect or during collection; or some (~50%) of the ^{133}Xe created from the ^{240}Pu in the tank never reaches the surface and is trapped for extended period in crystalline structure or in the waste form. Without further analyses, the dominate effect is difficult to determine and performing detailed analyses on Hanford tanks is extremely expensive. Finally, there are fundamental uncertainties in both the spontaneous fission per decay value (4.5 to 5.7x10^{-8}) and all the xenon isotope yields (7.23 to 8.35% for ^{133}Xe).

6.0 Conclusions

We have made measurements of radioxenon in headspace air from a waste tank at the Hanford site in Washington State known to hold ^{240}Pu and other transuranics. From previous measurements it is believed that the ^{240}Pu in the mixed waste dominates the spontaneous fission in the tank, and so we were able to calculate the mass of ^{240}Pu, after correcting for a number of effects. Our results are more than two-fold lower than the best-estimate inventory of ^{240}Pu mass determined from measurements of samples taken from the tank, though considering the significant uncertainty in both the best-estimate inventory and effects of passive venting of headspace air, our calculated mass is comparable to the expected value.

This proof-of-principle demonstration using ultra-sensitive radio-xenon gas measurements to determine ^{240}Pu inventory of a waste tank shows great promise. A more controlled exercise involving a better characterized tank would permit a better evaluation of the true capabilities. A more controlled exercise would involve a tank with an accurately known ^{240}Pu inventory, a known ventilation rate, and a waste form with a well understood Xe hold-up behavior.

7.0 References

Dresel PE and SR Waichler. 2004. PNNL-14617. "Evaluation of Xenon Gas Detection as a Means for Identifying Buried Transuranic Waste at the Radioactive Waste Management Complex, Idaho National Environmental and Engineering Laboratory." Pacific Northwest National Laboratory, Richland, Washington.

Olsen KB, DP Mendoza, VT Woods, and DA Haas. 2012. PNNL-21992. "Using Radioxenon Gas Sampling and Analysis Methods to Estimate Total Plutonium Content Within Facilities on the Hanford Site." Pacific Northwest National Laboratory, Richland, Washington.

Lestone JP. 2011. "Energy Dependence of Plutonium Fission-Product Yields." *Nuclear Data Sheets*. 112 (2011) 3120-3134. Elsevier

Dresel PE, KB Olsen, JC Hayes, JI McIntyre, SR Waichler, and BM Kennedy. 2008. "Environmental applications of stable xenon and radioxenon monitoring." *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 276, No. 3 (2008) 763-769.

Dresel PE, KB Olsen, JL McIntyre, BM Kennedy, JC Hayes, DG Horton, AV Mitroshkov, and ME Panisko. 2003. "Xenon Isotopes in Soil Gas as Indicators of Buried Radioactive Waste [abstr]." *Geol. Soc. Am. Annual Meeting*, Seattle, Washington.

England TR and BF Rider. 1994. ENDF-349. *Evaluation and Compilation of Fission Product Yields 1993*. LA-UR-94-3106, Los Alamos National Laboratory, Los Alamos, New Mexico.

Holden NE and DC Hoffman. 2000. "Spontaneous Fission Half-Lives for Ground-State Nuclides." IUPAC Pure Appl. Chem, Vol. 72, no. 8, pp. 1525-1562.

McIntyre JI, KH Abel, TW Boyer, JC Hayes, TR Heimbigner, ME Panisko, PL Reeder, RC Thompson. 2001. “Measurements of ambient radioxenon levels using the automated radioxenon sampler/analyzer (ARSA).” *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 248, No. 3, pp. 629-635.

Parrington JR, HD Knox, SL Breneman, EM Baum, and F Feiner. 1996. *Nuclides and Isotopes*, Fifteenth edition. General Electric Co. and KAPL, Inc. San Jose, California

U.S. Department of Energy (DOE). 1996 Plutonium: The First 50 Years. DOE/DP-0137, U.S. Department of Energy, Washington, D.C.

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