OBSERVED TRU DATA FROM NUCLEAR UTILITY WASTE STREAMS

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ABSTRACT

TMA/Norcal has performed 10CFR61 analysis of radioactive waste streams from BWR's and PWR's since 1983. Many standard and non-routine sample types have been received for analysis from nuclear power plants nation-wide. In addition to the 10CFR61 Tables I and II analyses, we also have analyzed for many of the supplementary isotopes. As part of this program, TRU analyses are required. As a result, have accumulated a significant amount of data for plutonium, americium, and curium in radioactive waste for many different sample matrices from many different waste streams.

This paper will present our analytical program for 10CFR61 TRU. The laboratory methodology including chemical and radiometric procedures is discussed. The sensitivity of our measurements and ability to meet the lower limits of detection is also discussed.

Secondly, a review of TRU data is presented. Scaling factors and their ranges from selected PWR stations are included. We discuss some features of, and limits to, interpretation of these data.

INTRODUCTION

10CFR61 of the Licensing Requirements for Land Disposal of Radioactive Waste under Par. 61:55, Waste Classification, (1) requires that alpha emitting transuranic nuclides in rad waste with a half-life greater than five years, as well as shorter-lived ^{242}Cm be analyzed. This information is then used to determine the concentration and to calculate the waste classification. Virtually all of the rad waste to be analyzed derives from the nuclear fuel cycle. Samples received are from radwaste streams, fuel pools, decontamination programs, decommissioning sites, etc. In general, the major proportion of our samples are from BWR's and PWR's and they have been analyzed for all of the 10CFR61 TRU radionuclides, Table I.

As a radiological analysis laboratory, we receive a large variety of high and low level samples collected on, or consisting of, a large variety of matrices from many different waste streams from BWR's and PWR's. The TRU analyses must be performed so as to be representative of the submitted sample, with good precision and accuracy, or within our target sensitivities or LLD's, Table II.

The wide range of sample activities presents a problem. For instance, if the sample has a higher level of $^{239,240}Pu$, such as 40. Bq/g (10^{-3} μCi/g), the analysis could be performed with good precision on a milligram of sample. However, most often, much more than a milligram of sample is needed for a representative aliquot, typically several thousand times more (several grams) must be dissolved and prepared for analysis. Another sample in the same batch may be at a $^{239,240}Pu$ level of 0.04 Bq/g (10^{-6} μCi/g), several, or tens or more grams of sample must be dissolved. If the processing were done blindly, it would be possible to be processing unknown sample aliquots, side-by-side, one with 400. Bq/g $^{239,240}Pu$ (10,000 pCi) and the other with 0.4 (10. pCi). There would be a great possibility for cross contamination of these sample analyses, other samples, the laboratory, or sensitive counting equipment. Also, unexpectedly high levels of TRU's can swamp added tracers and ruin an analysis. An additional problem is that other non-transuranic radioactivity in each sample may be high or low, independent of the TRU. This is indicated by the $^{239,240}Pu/^{60}Co$ scaling factor distribution, which may range from 10^{-3} to 10^{-7}. Total activity per sample at the laboratory is generally limited to 70. Bq beta gamma (2000. pCi), 4. E+04 Bq/g (1. μCi) alpha emitting TRU, and a dose rate of 1.1 E-06 Gy/s (400 mR/hr) at the surface by ionization chamber measurement.

Activity control in TRU analyses is by use of three laboratory areas: high, intermediate, and low level. These are utilized in conjunction with appropriate sample processing plans, wherein representative high level samples are prepared and dissolved but, reduced levels of TRU are aliquoted for analysis, so there is a more even match with large aliquots from low level samples. Initial purifications are performed, aliquots are appropriately merged for final processing and only lower level purified individual TRU plates are measured in the alpha spectrometers.

In order to obtain our goals, incoming samples are reviewed and categorized according to certain characteristics. Our interest in TRU scaling factors is to aid in this process and the scope of this paper is limited to this purpose and a limited presentation of these factors. Since there are such a wide range of possible TRU results, the industry-wide scaling factors given by the works of Best (2,3), Cline (4), and others, are not necessarily of use in our work. Although, in the course of our work, we have obtained a wealth of data, an exhaustive detailed review is beyond our scope, and the application and interpretation on an indus

TABLE I
TYPICAL SAMPLE TYPES ANALYZED AT TMA/Norcal

BWR's

Reactor water
Evaporator bottoms
Waste receiver tank liquid
Reactor water filter
Condensate resin
Bead resins
RWCU resins
Floor drain, demin. resins
CWPS resin
Powder resin
R_x CU resins
Spent resin tank sample mixture
Concentrator waste sludge
Water sludge
Clean up sludge
Oils, all types
Laundry decon sump
PWR's
RCS coolant
MWST coolant
Evaporator bottoms
RCS crud filter
CVCS filter
Seal rebuild filters
Bead resins
Deborating resins
Powder resins
ADT resin
Condensate resin
R_x CU resins
Turbine building smears composite
Reactor building smears composite
DAW smears
Filter smears
SFP sludge
SFP vacuum bag composites
SFP stainless steel activation products
SFP stainless steel surface activity
Zircalloy metal activation products
Zircalloy metal surface activity
In core metals, various
Many others
Contaminated oil
Charcoal
Filter sludge
DAW composites
Smears (plant DAW)
Wipes of filter cartridges
Sump, change room wipes
ICI thimble
SFP metal shavings
Diatomaceous earth
Mophead strings
Shot peening powder
Compactable non-compactable solids
Many others

try-wide basis for waste classification purposes is already being done by others.

SUMMARY OF METHODS

The procedures for the analysis, (Refs. 5,6,7, and 8) of alpha-emitting transuranics consist of a dissolution procedure followed by a tracer equilibration. Appropriate separations and purifications are performed, after which the TRU element is prepared as a weightless carrier free electrodeposite on a stainless steel disc. Radiometric assay is by alpha spectrometry. The spectrum is taken on one of a number of 450. mm^2 surface barrier diodes over the energy region 3.64 to 7.00 MeV, The spectrum is spread over 256 channels and counted for a 60,000-second (1,000-minute) period in, most cases. Each detector is energy-calibrated with standards and detector backgrounds are determined periodically as part of an instrument QC program. Results are calculated by computer programs. Efficiencies vary from 25 to 33% and backgrounds from 0 to 10 counts per 60,000-second measurement. The final activity for each isotope is determined by ratio calculation against the amount of tracer added.

The alpha-emitting transuranics of interest include ^{237}Np, ^{238}Pu, $^{239,240}Pu$, ^{242}Pu, ^{241}Am, ^{242}Cm, and $^{243,244}Cm$. The yield tracers which are used for the analyses are ^{239}Np for Np, ^{236}Pu for Pu, and ^{243}Am for both Am and Cm

TABLE II

Detection Limits For Transuranic Analyses (Bq/unit aliquot* Isotopes

Sample and Unit	^{237}Np	^{238}Pu	^{239}Pu	^{241}Pu	^{241}Am	^{242}Cm	^{244}Cm
Coolant Bq/mL	1.-05	7.-06	7.-06	4.-04	7.-06	7.-06	7.-06
Low Level Resin Bq/g	2.-03	1.-03	1.-03	1.-01	1.-03	1.-03	1.-03
High Level Resin Bq/g	1.-02	7.-03	7.-03	4.-01	7.-03	7.-03	7.-03
Smears Bq/total	2.-02	7.-03	7.-03	4.-01	7.-03	7.-03	7.-03
Oils Bq/mL	7.-05	7.-05	7.-05	7.-03	7.-05	7.-05	7.-05

* 1 Bq = 2.70 E-05 μCi. Format example 1.-05 equals 1. E-05.

isotopes. If it suspected that the analyses is perturbed by the presence of a tracer isotope in the sample, a suitable reanalysis can be performed and the results recalculated appropriately. For example, ^{245}Cm alpha emissions would visibly interfere with the resolution of the tracer ^{243}Am, but could be dealt with by either reanalyzing at a smaller aliquot, which would not have enough ^{245}Cm to interfere, or reanalyzing with a tracer-free aliquot to determine quantitatively how much ^{245}Cm is present in the sample. Appropriate calculations would then be done to determine the concentrations of the other Am and Cm isotopes.

A brief summary of the radiochemical procedures for each element is outlined below.

Np: Ion exchange purification, TTA extraction, plating a nd beta count decay of ^{239}Np for yield, 2π alpha counting plus alpha spectrometer purity check.

Pu: Two or more ion exchange purifications, then plating and alpha spectrometry.

Am-Cm: Anion exchange, oxalate, hydroxide and fluoride precipitations, anion and cation exchange separations from rare earths, then plating and alpha spectrometry.

^{243}Am: This isotope can also be determined by isotope dilution alpha spectrometry. A second analysis is done without added ^{243}Am tracer. Since it is expected to be present at insignificant levels, it is rarely ordered. However, if a significant amount of ^{243}Am is indicated, it can be positively identified and measured by tracer-free chemistry and alpha spectrometry, as an option, or its effect on the tracer in a ^{241}Am, ^{242}Cm, and ^{244}Cm analysis can be eliminated by reanalysis with revised input parameters.

^{241}Pu: The plated Pu disc from the alpha analysis is further processed. The Pu is dissolved off of the plate, completeness may be checked by alpha counting the stripped plate. The Pu is extracted into a combined extractant-cocktail solution and counted several times on a liquid scintillation spectrometer. The ^{241}Pu beta counts are corrected for alpha interference and yield. The method is standardized by counting ^{241}Pu and $^{239,240}Pu$ standards and blanks with each set.

Several factors could limit the laboratory's ability to meet the target LLDs. Isotopic interferences are an important constraint for some analyses. For example, any residual beta gamma activity may interfere with the LSC counting for ^{241}Pu. High decontamination is a goal, sometimes, with some sacrifice in lower chemical recoveries. This problem applies to the ^{237}Np analysis, also, because of the use of beta-emitting ^{239}Np as a tracer and the very high levels of other beta emitters which must be separated.

Another isotopic interference is the overlap of peaks on an alpha spectrum of different TRU's. Plutonium-238 and ^{241}Am interfere, as do tracer ^{236}Pu and ^{242}Cm, for

example. These interferences can be important at very low activity levels. Just a few counts in a 60,000 second count of an interfering isotope could significantly alter the LLD calculation. Therefore, as in the previous example, very high decontamination levels are required for the separation chemistry.

Matrix interferences are another consideration. There is great variability for some sample types in the amount of material and in the chemical nature of this material. We have analyzed oil samples that range from less than 1% ash to greater than 50% ash composition. This greatly affects the size of the aliquot we can take.

The varied chemical composition of samples frequently requires the employment of special decontamination procedures. High metal content in some resins, high sulfates and borates in concentrates, and anomalous sample types, e.g., activated metals, concrete, etc, are some examples. Each requires individualized chemical procedures for each radioisotope analyzed from such samples.

Other parameters affecting the LLD achieved are programmatic. On occasion, not enough sample is sent and no more is available, so reduced aliquots may cause a sacrifice of sensitivity. In other cases, we receive smear composites with hundreds of individual smears. For these, sometimes the aliquots are limited by mass of mineral ash, so that the fractional aliquots are correspondingly reduced. Client requests for rapid turn-around does not normally affect our ability to meet target LLDs. Through better organization and coordination, forseeable problems can be prevented from interfering with the process.

TRU's IN SELECTED SAMPLES

We have analyzed 10CFR61 samples from a large number of nuclear power stations. However, five were selected for review. Two are newer stations and have a large number of samples, starting with the first 10CFR61 samplings to present. Three are older stations, which have a large number of samples, either starting with the first 10CFR61 samplings in 1983, or else several years of samplings to the present time. A wide range of TRU scaling factors have been obtained for each station, as shown in Table III.

The basic correlations or scaling factor ratios are $^{239,240}Pu/^{60}Co$ or $^{239,240}Pu/^{137}Cs$. Some samples are depleted in either ^{60}Co or ^{137}Cs and, due to high level interferences in the gamma spectroscopy method, only detection limits can be obtained. In most such cases, positive measurements can be obtained by interference-free radiochemistry, plus gamma spectroscopy. Some data users consider a detection limit for these key isotopes to be acceptable for use in scaling factors, etc., but others require the more useful radiochemistry data. Cerium-144 is not used in this review because it is often below detection limits, due to high level interferences in direct gamma spectroscopy. Cerium-144 results by interference-free radiochemistry extend to much lower LLD's but, ^{144}Ce was not always ordered. Also, the 281-day ^{144}Ce decays to negligible levels in aged samples and or the time dependency of the scaling factor adds uncertainty when samples contain unknown sources. This revue is limited to positive values, i.e., greater than MDA, for $^{239}Pu/^{60}Co$ as a primary scaling factor. The other TRU's, ^{238}Pu, ^{241}Pu, ^{241}Am, ^{242}Cm, and $^{243,244}Cm$ are scaled to the ^{239}Pu base. Plutonium-242 is not discussed, since it is present in very low abundance and is difficult to resolve by alpha spectroscopy from high levels of ^{239}Pu. Also, there is a slight interference from the minor alpha branches of ^{241}Pu decay.

Categorization of Sample Activities - Total Gamma and ^{60}Co

The radioactivity per sample varies greatly among the various samples submitted by each station. The use of total gamma activity, i.e., Bequerels (μCi) of gamma emitters per gram, or other unit, has not turned out to always be a reliable indice for correlating the samples and work plans. A sample which contains short-lived activity, may have decayed considerably by the time it arrives at the laboratory. More detailed information, i.e., activity of ^{60}Co, ^{137}Cs, and other prominent gamma emitters is more useful, used by itself, or in conjunction with the total gamma activity.

The ^{60}Co activity is one of the most useful indices for planning. The range of ^{60}Co activity, per unit of measure, varies greatly for each reactor, either old or new, from a low limit of 0.004 to 0.04 Bq/unit (0.1 to 1. E-06 μCi/unit) up to a high limit of 1. E+5 to 6. E+06 Bq/unit (3. to 150. μCi/unit). Samples from the older station D have never exceeded 1. E+05 Bq/^{60}Co/g (3 μCi/g).

Plutonium-239 Scaling Factor - $^{239}Pu/^{60}Co$

Although the total of ^{239}Pu + ^{240}Pu is always measured in alpha spectrometry analyses. Plutonium-239 is usually used in scaling factor discussions, as in Best (2), even though on an activity basis, ^{240}Pu may exceed the activity of longer-lived ^{239}Pu.

The ^{239}Pu value, scaled to ^{60}Co varies widely in waste streams at each station, but as shown in Table III, the upper and lower limits at the different stations are approximately the same. The $^{239}Pu/^{60}Co$ ratios are within the range of 4. E-03 as a high, and 2. E-07 as a low value. An exception is the newer station B, with a shorter range of 3. E-05 down to 3. E-08, but there is an increasing trend in the ratio.

If ^{60}Co is depleted in the sample and has not been measured by direct gamma, the planning must be done by other criteria. Even if a ^{60}Co radiochemistry analysis is started, the information is rarely available before TRU analyses. In one such instance, the radiochemistry method

TABLE III

Ranges of TRU Scaling Factors in Selected PWR Station Samplings (1)

STATION (2)	$\frac{^{239}Pu}{^{60}Co}$	$\frac{^{238}Pu}{^{239}Pu}$	$\frac{^{241}Pu}{^{239}Pu}$	$\frac{^{241}Am}{^{239}Pu}$	$\frac{^{242}Cm}{^{239}Pu}$	$\frac{^{244}Cm}{^{239}Pu}$
A (Newer)						
High	4. E-03	2.7	100.	1.8	14.	1.6
Low	5. E-07	0.09	25.	0.04	1.3	0.03
B (Newer)						
High	3. E-05	0.8	52.	0.2	0.8	0.04
Low	3. E-08	0.2	19.	0.04	0.4	0.004
C (Older)						
High	1. E-03	0.9	95.	0.2	4.	1.4
Low	2. E-07	0.15	33.	0.9	0.2	0.03
D (Older)						
High	1. E-03	3.1	196.	3.5	10.	3.
Low	2. E-06	0.1	36.	0.2	0.2	0.04
E (Older)						
High	1. E-02	4.4	184.	3.6	36.	6.7
Low	2. E-06	3.0	73.	0.4	0.2	0.5
Best (3), all samples	1.6 E-04(11)	0.83(7)	99(2)	0.40(9)	0.43(8)	0.45 (27)
High (Liquids)		5.1 E-04 (52.)				
Low (Resin)		1.7 E-05 (3.)				
High (Filters)						0.42 (5.9)
Low (Resin)						0.03 (6.4)
Best (4)						
200 day	----	0.152	33	7.2 E-03	5.1 E-01	1.14 E-03
500 day	----	0.65	97	5.5 E-02	9.6	8.3 E-02
900 day	----	1.89	145	1.3 E-01	37	1.09

(1) ^{239}Pu means $^{239,240}Pu$, ^{244}Cm means $^{243,244}Cm$.

(2) Multi-unit stations, new or old, as indicated.

(3) Best (2) p 4-5 and 4-6, Ratio (± Log Mean Dispersion).

(4) Best (3) p 5-25 Ratio abstracted for 200, 500, and 900-day irradiation of typical PWR fuel. Although not stated, it is assumed the ratio is for pure ^{239}Pu rather than $^{239,240}Pu$.

showed the ratio $^{137}Cs/^{60}Co$ was 2,000. The $^{239,240}Pu/^{60}Co$ scaling factor was 3. E-04, whereas, using the higher direct ^{60}Co MDA, the factor was <1. E-04, which would give considerably more errors in the estimates for TRU's in the waste.

In the case of one oil sample, ^{60}Co was not detectable by direct gamma spec at <1. E-07 μCi/mL, however, sensitive measurements showed slightly positive TRU levels for isotopes within the expected range of TRU scaling factors. Such a sample has to be analyzed in a low level laboratory.

Scaling Factors for $^{238}Pu/^{239}Pu$

The range of $^{238}Pu/^{239}Pu$ scaling factors is variable at each reactor station for various reasons. The overall range is a high of 3.0 and a low of 0.09. However, the detail of the factors at each station vary considerably from those values. The older station E has the shortest and most consistent set of scaling factors, 3.0 to 4.4. The variations in the $^{238}Pu/^{239}Pu$ ratio do not affect our analyses except that a sample with a high ratio can easily perturb the ratio in a low level sample through cross contamination, if processing is not carefully controlled. The high ratios of $^{238}Pu/^{239}Pu$ in reactor waste also present an even greater contamination hazard to other Pu analyses in the lab where $^{238}Pu/^{239}Pu$ may range down to ratios of 1. E-02 or 1. E-03. Analyses are segregated and control is evaluated through blanks and standards.

Scaling Factors for $^{241}Pu/^{239}Pu$

The overall range of $^{241}Pu/^{239}Pu$ scaling factors in Table III is from 196 down to 25. The older stations have the higher values, as might be expected. However, there is also a variation at all stations for the various samplings, indicating various sources of Pu.

Scaling Factors for $^{241}Am/^{239}Pu$

The $^{241}Am/^{239}Pu$ scaling factors in Table III range from a high of 9.1 down to 0.04. Station C, once again, has the shortest range and lower values, while the detailed factors for Station E shows an overall higher ratio but, with only a few as low as 0.4.

The ^{241}Am activity level is an important consideration in our analysis. If the ^{241}Am activity is too high in the aliquot analyzed, it may perturb the analysis results, or it may ruin the analyses. This is an analysis, in which both ^{241}Am, ^{242}Cm, and ^{242}Cm are determined at the same time. It requires very extensive and complex chemistry purification. The ^{241}Am alpha peak has a primary alpha energy at 4.49 MeV and tailing into the lower energy ^{243}Am tracer peak at 4.26 MeV on the alpha spectrum can perturb, or ruin, the analysis. Since high purity ^{243}Am tracer is scarce, usually only 0.2 Bq (5 pCi) of ^{243}Am is used per analysis. It is preferable to have the ^{241}Am activity no higher than 4 times the tracer level, although this can be extended several times with good analytical technique. Since there is a wide variation of the two factors $^{239}Pu/^{60}Co$ times $^{241}Am/^{239}Pu$, educated guesses, and intuition, as well as scaling factors aid in selecting the best aliquot for accurate analyses.

Scaling Factors for $^{242}Cm/^{239}Pu$

The range of $^{242}Cm/^{239}Pu$ scaling factors is 0.2 to 36. Some samples received at the laboratory are six months, even as much as a year old. The results reported include a correction for radioactive decay back to the sample date. For 163-day ^{242}Cm, the 6-month correction is a factor of two. The unknown decay factors included in a series of ^{242}Cm scaling factors may distort the overall pattern and affect conclusions on trends, etc.

Scaling Factors for $^{244}Cm/^{239}Pu$

The range of $^{244}Cm/^{239}Pu$ scaling factors in Table III is from 0.004 to 6.7. Station B has the shortest and lowest range. Station E has the highest maximum and the variation among samples is less with mostly high ratios.

SUMMARY

The TRU scaling factors in five selected PWR stations fall within the industry-wide data ranges. The industry-wide PWR TRU scaling factors from Best (2) are listed in Table III, for comparison. The values are within most of the range limits, considering that the errors for the industry-wide data are listed as the $\pm$ log mean dispersion values.

Isotope ratios calculated by Origen-2, as a function of irradiation period for a typical PWR fuel are given by Best (3). The values, or theoretical TRU scaling factors for 200, 500, and 900-day periods are listed in Table III for a ballpark comparison. From a limited review, it appears that the analyses we selected to review do not follow the time pattern of that tabulation. The TRU data which we measure do not contain single pure TRU irradiated sources. The samples may be from individual and/or mixed samples from one or more reactors at the station as well as samples form different operating conditions.

There is a considerable variation of TRU scaling factors at each of the stations among the many samples analyzed, even among different samples collected at a station at the same time. Since this review is made from the analytical laboratory's point of view, no conclusions are drawn for the effect on waste classification at these stations,

which have good records of TRU data upon which to base their program.

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