ASSAY OF SOLIDIFIED RADWASTE

H. R. Helmholz
NWT Corp.

M. D. Naughton
EPRI

INTRODUCTION

A wide variety of solid radioactive waste material is generated at nuclear power plants. The primary classes of wastes are (1) spent ion exchange resins, (2) solidified waste concentrates, (3) compacted plastic and paper, (4) cartridge filters and filter media, and (5) scrap metal, piping and components. This diverse array of waste materials coupled with wide variations in contamination levels presents significant assay difficulties.

Since regulatory requirements related to storage and disposal of solid radioactive waste are becoming increasingly restrictive, the accurate determination of isotopic composition and curie content of solid wastes is assuming added importance. Recognizing this, EPRI funded RP 1568-1 in March 1981 to review the radioactive assay processes associated with the determination of the curie content and radionuclide composition of nuclear power plant solid radwastes. The study included a review of present practices at nuclear plants including identification of waste materials, common waste geometries, common radionuclides, sampling techniques, counting schemes, monitoring instruments, and methods of calculation. The regulations, guides, and burial site requirements as well as proposed revisions were reviewed to determine their impact on existing waste assay methods. Fifteen sites were visited for an in-depth review of their radwaste operation and radioassay methods.

This paper presents some of the significant findings of this study. Because of the potential impact of 10 CFR 61 on reactor operations, a significant portion of this paper is devoted to a discussion of this regulation from a nuclear chemist's viewpoint.

Waste Sampling and Analysis

The review of plant practices showed a universal belief that the primary criterion for shipping purposes is the package radiation level at contact and at 3 ft, as specified by the Department of Transportation. The overwhelming emphasis is to make certain that none of the many possible audits of the radiation levels by compliance people results in a higher reading than recorded on the shipping papers. The curie content is considered to be of secondary importance. The following general methods are used for waste analysis and to determine the total curie content of waste packages:

1) Quantitatively analyze a sample of the waste and multiply by the quantity of waste transferred to the shipping container. Potentially this is the most accurate method. The difficulty is that except for liquid streams, minimal sampling capability has been designed into the radwaste systems, and even where the capability exists it is often impossible to obtain a representative sample. A modification of this method is to sample the influent and effluent streams across a filter or demineralizer and to use the difference for calculating the retained activity.

2) Measure the package dose rate and calculate the curie content. A grab sample, a smear, analysis of similar material, or inference is used to obtain the fractional nuclide distribution. The total curie content calculated from the dose rate is multiplied by the fractional distribution to obtain the quantity of each nuclide.

3) Use special analyses and outside laboratories to develop correlations between species not normally measured and nuclides which are readily measured at the plant. This technique is being widely applied to estimate plutonium activity, and in some cases the activity of pure beta emitters.

Plant waste analyses are limited almost entirely to analysis of gamma emitting nuclides by gamma ray spectroscopy. All plants use germanium detectors with sophisticated computer programs to reduce the data. In general, the analysis capability far exceeds the sampling ability. Since the waste assay is based only on the observed nuclides, there is a wide variation in reported nuclides depending on failed fuel status and age of the wastes. For example, some plants store reactor clean-up resins for 1 to 2 years

prior to processing. Others have a hold-up capacity on the order of 1 to 2 months. At the extreme, the latter reports only I-131 Ba/La-140, and other nuclides of similar half-life, while the former reports Cs-137, Co-60, Mn-54, etc.

It is difficult to offer general comments about waste packages. Some plants ship most of their wastes in 55-gallon drums, while others use liners of several hundred cubic feet capacity. Resins, which are used in various locations, are either solidified or dewatered for disposal. Some sites blend,all expended resins in a spent resin storage tank. Others segregate the resins, and even at the same site may process and package these resins by different means.

Almost all sites now compact contaminated trash in 55 gallon drums. A few are surveying packing materials, etc. and disposing of the trash with nondetectable activity as ordinary waste. All PWR's use filter cartridges in the reactor let-down systems and in many other plant locations. These can contain high levels of activity and are extremely difficult to sample. On the other hand, all BWR's use only filter media and/or demineralizer resins in the reactor clean-up systems. Filter cartridges are rarely used at any point in BWR systems.

Dose Rate to Curie Conversion

All sites perform dose rate to curie content conversions to one extent or another. At one extreme, this conversion is applied only to trash and contaminated scrap; at the other extreme it is applied to all solid waste packages. The activity level of the package is not the governing factor in the choice of this method, but rather it results from the heterogeneity of the package, the uncertainties in the quantity of waste transferred to the container, or the inability to obtain a representative sample. If the activity level has an impact on this choice, it is primarily that the dose rates impose limitations on sampling capability. In most cases, dose rate readings taken for shipping purposes also form the basis of the dose rate to curie calculations. Treatment of the data for the purposes of calculating the dose rate varies from site to site. Some use average readings; others use maximum readings. Some use the contact reading; others use the three-foot reading or occasionally some other reference distance. A few use the average reading for calculating the curie content and the maximum reading for shipping purposes.

Various methods are used to obtain dose to curie content conversion factors. These vary from rule-of-thumb factors to detailed computer processed tables of curie content versus dose rate for individual package types and densities. Factors also have

been determined empirically from observed dose rates on containers filled with measured quantities of activity. Generally, the intent has been to be certain that the curie content is not understated, and the calculations are conservatively biased on the high side. As an example, in one case a constant of 4 mCi/(mR/h) is employed, even though radiochemical analyses have confirmed that the factor should be 2.6. Usually, conversion factors are based on point kernel calculations of the expected dose rates from the various size containers. Several computer programs have been developed for these calculations. The two most commonly used are ISOSHLD[1] and QAD.[2] In addition, there are the general equations and parametric values given in Rockwell's "Reactor Shielding Design Manual"[3] and the "Radiological Health Handbook",[4] both of which are widely used as a starting basis. Bowman and Swindle have published parametric curves[5] for determining surface dose rate to curie content as function of container diameter based on Rockwell's manual. These curves are used by many sites.

An accurate determination of the curie content requires that the dose rate conversion factor be based on the activity of each individual nuclide, its gamma energies and the number of photons per decay at each energy. Most sites have simplified this determination by either assuming a 0.75 mev average gamma energy with one gamma per decay or assuming the average 1.25 mev gamma energy of Co-60. A series of conversion constants are then tabulated for each size shipping container and for each major density, e.g., concrete wastes, dewatered resins, and compressed trash. Some sites which employ the services of a waste handling group to process their wastes rely on the vendor to supply conversion factors for their liners.

Transuranic Analysis

On September 12, 1974, the AEC published a proposed regulation to limit the burial of wastes contaminated with transuranic activities to 10 nCi of transuranics per gram of waste.[6] This regulation was never enacted by the Federal government, but was adopted by the three states having licensed burial sites. The original proposal compared the hazards of 24000 y Pu-239 to 1600 y Ra-226, and the intent was to limit long-lived alpha activity in wastes to the average radium activity in the earth's crust. In actuality, after the first few months of initial reactor operation the alpha activity of the primary coolant is 90-95% 163 day Cm-242 with some 18.1 year Cm-244. Approximately 90% of the plutonium alpha activity in the fuel at the time of discharge is 87.1 year Pu-238, while approximately 90% of the total plutonium activity is due to beta emitting 14.7 year Pu-241.[7] The genesis of the transuranics is shown in Fig. 1. Actual composition in the

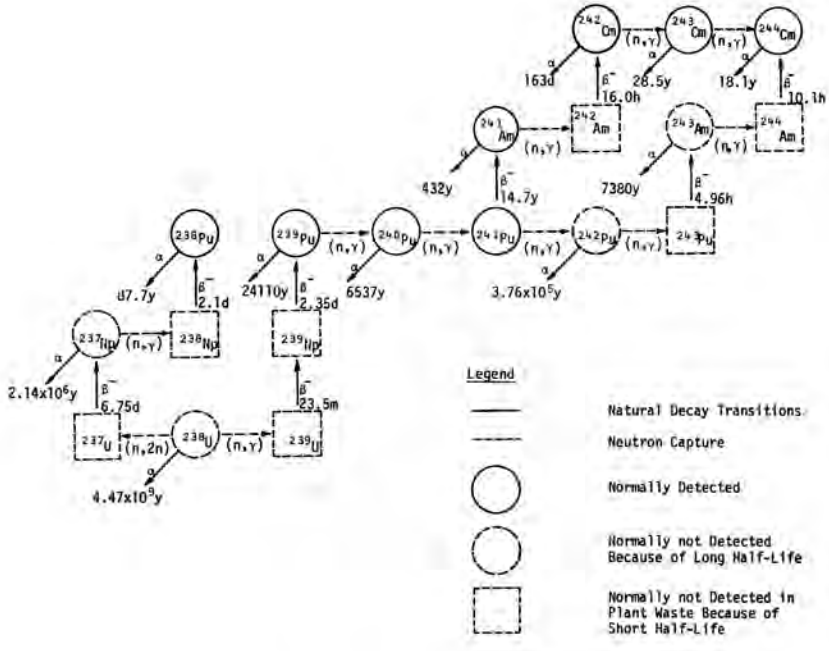

Fig. 1. Genesis of the Transuranics

plant wastes will depend on the age of the waste, the mechanism of release from the reactor fuel, and the average age of the fuel. The alpha activity will be mostly 24,000 year Pu-239 only if there is no holdup of the uranium activation products following initial neutron capture in the U-238.

In 1976, the Electric Power Research Institute (EPRI) funded Science Applications, Incorporated (SAI), to conduct a study of transuranic nuclides in power plant wastes.[8] As an alternative to involved chemical separations and alpha energy analysis, SAI demonstrated a correlation of $(1.8 \pm 1.0) \times 10^{-3}$ μCi of Pu-239 plus Pu-240 per μCi of 284 day Ce-144. It was suggested that analysis of the solid wastes for Ce-144 would permit estimation of the plutonium activity within a factor of three. Since there was considerable variation both between plants and between waste forms, it was recommended that each site develop its own correlation approximately yearly.

To comply with the burial site limits of 10 nCi/gram and demonstrate compliance with this limit to NRC inspectors, three sites have used SAI's correlation to estimate the plutonium activity. Six sites send out samples for annual or semiannual analysis to support the Ce-144 correlation. Of these, one has sent out its first samples and has yet to receive its results, one plans to send out samples, and one sent out samples and obtained uranium isotopic analyses instead of transuranics. Two sites have claimed no failed fuel and, therefore, insignificant transuranics levels. Two claim insignificant transuranic levels based on coolant gross alpha activity; two sites have not addressed the issue. None of the sites visited in this study have had problems in disposing of solid wastes on the basis of transuranic levels. Although certain concentrations of the waste streams exceed the 10 μCi per gram limit, blending of such wastes with other wastes leads to mixtures below the limit. At the recent Radwaste Radioassay Workshop, it was pointed out that there is one site which is having to store reactor coolant resins because of the transuranic level; they are also having difficulty in disposal of their reactor coolant filter cartridges.[9]

PROPOSED 10 CFR 61

On July 24, 1981 the NRC published in the Federal Register a proposed rulemaking, 10 CFR 61, pertaining to the land disposal of radioactive wastes.[10] This regulation will impact on power reactors through the technical requirements concerning waste forms, shipping records, waste classification, and quality assurance that waste generators must meet for land disposal of wastes. To meet its objectives with respect to burial site boundary doses and inadvertent intruder exposure following cessation of operations,

the NRC defined four classes of wastes based on half-life, quantity of activity, and pathway models.

The concentration limits for these classes are given in Table I. Wastes whose concentration of long-lived nuclides exceeds those of Class C Intruder wastes are not acceptable for near surface burial and must be disposed of by as yet undefined methods. Tables II and III summarize the nuclear decay characteristics and production modes, respectively, of these nuclides. It should be noted that the production modes of H-3 and C-14 are significantly different that those given in the data base for 10 CFR 61.[11] Many of the listed nuclides are pure beta emitters. Furthermore, concentrations of many of these nuclides are insignificant relative to other activities in power plant wastes. In some cases, the only alternative to mass spectrometric analysis will be to develop correlations between the desired nuclides and those which are more readily measured. It is believed that Cs-137, Sr-90, and the transuranics will be the limiting nuclides for disposal of power plant wastes. Since these nuclides usually occur in the same waste streams, the allowable concentrations of the individual species may be significantly lower than those listed. The prohibition on waste containing chelating agents in concentrations greater than 0.1% means that in some cases decontamination solutions must be decomposed prior to disposal.

At present, analyses are performed routinely for Co-60 and Cs-137 in wastes. It is within the capability of the power plants to analyze for Sr-90 and Ni-63. Comments with regard to analyses for the other nuclides listed in 10 CFR 61 are as follows:

1) The H-3 concentration in reactor wastes cannot be highe than that in the reactor water. The amount of tritium in the waste, therefore, can be bounded by the reactor water concentration and the percent water in the waste.

2) There are reasons for believing that C-14 is eliminated primarily as a gaseous waste. If not, the production rate is sufficient to make it a limiting nuclide in solid wastes.

3) Ni-59 can be estimated on the basis of Ni-63. Both are long-lived and hopefully Ni-59 can be deleted from analysis as Ni-63 should be more limiting.

4) Production of Nb-94 is limited to neutron capture in niobium impurities. Its analysis, or estimation, should be limited to the disposal of items constructed of zirconium.

Table I. Waste Classification Activity Limits[a]

Nuclide	Class A Segregated (uCi/cm^3)	Class B Stable (uCi/cm^3)	Class C Intruder (uCi/cm^3)
Half Life <5 years	700	70,000	Max. spec. act.[b]
H-3	40	10^8	Max. spec. act.[bcd]
C-14	0.8	0.8	0.8[bcd]
Ni-59	2.2	2.2	2.2
Co-60	700	70,000	Max. spec. act.[b]
Ni-63	3.5	70	70
Nb-94	0.002	0.002	0.002
Sr-90	0.04	150	700
Tc-99	0.3	0.3	0.3[c,d]
I-129	0.008	0.008	0.008[c,d]
Cs-135	84	84	84
Cs-137	1.0	44	4600
Enriched U	0.04	0.04	0.04
Nat. or Depleted U	0.05	0.05	0.05
Alpha Emitting Transuranics	<10 nanocuries per gram all classes[e]		
Pu-241	<350 nanocuries per gram all classes		

a) Concentrations may be averaged over package; chelating agents concentration must be less than 0.1%; the sum of the fraction of the limits for each nuclide must be less than 1.

b) Specific activity of the pure nuclide. No upper limit.

c) Total activity of these nuclides in each package must be shown on the shipping manifest.

d) Disposal site will be limited to a total quantity buried at the site.

e) It has been stated that this applies to nuclides with half-lives >5 years. This eliminates the problem of 163 day Cm-242.

Table II. Nuclear Characteristics.

Nuclide	Max. Beta Energy Mev (%abundance)	Gamma Energy Mev (%abundance)
12.35 year H-3	0.0186 (100)	No gamma
5730 year C-14	0.155 (100)	No gamma
7.5×10^4 year Ni-59	Electron capture	No gamma[a]
100.1 year Ni-63	0.0659 (100)	No gamma
5.27 year Co-60	0.318 (100)	1.172 (100) 1.333 (100)
2.03×10^4 year Nb-94	0.473 (99)	0.7026 (98) 0.8711 (100)
28.82 year Sr-90	0.546 (100) 2.288 (100)[b]	No gamma No gamma[b,c]
2.14×10^5 year Tc-99	0.292 (100)	No gamma[c]
1.57×10^7 year I-129	0.150 (100)	0.040 (4)
2.95×10^6 year Cs-135	0.205 (100)	No gamma
30.17 year Cs-137	0.512 (94) 1.176 (6)	0.6616 (84.5)[d]

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a) Detectable only by Co-59 x-rays and small amount of internal bremstrahlen.

b) From 64.1 hour Y-90 daughter activity

c) Gamma transitions exist but less than 1×10^{-5}% abundance

d) From 2.55 minute Ba-137m activity

Table III. Nuclide Formation.

Nuclide	Production Mode	Class A Limit ($\mu Ci/cm^3$)	Comment
H-3	Li-6 (7.5%) (n,α), σ_α 940 b H-2 (0.15%) (n,γ), σ_γ 0.52 mb	40	ANSI-237, PWR coolant 1.0 μCi/g ANSI-237, BWR coolant 0.01 μCi/g
C-14	O-17 (.03%) (n,α), σ_α 0.24 b	0.8	Estimated Production 10-14 curies per year
Ni-59	Ni-58 (68.3%) (n,γ), σ_γ 4.6 b	2.2	Ni-59:Ni-63 Produced Activity 0:31:1, 10 CFR 61 limits 0.63:1
Ni-63	Ni-62 (3.6%) (n,γ), σ_γ 14.2 b	3.5	
Co-60	Co-59 (100%) (n,γ), σ_γ 36 b	700	
Nb-94	Nb-93 (100%) (n,γ), σ_γ 1.13 b	0.002	From Nb-93 in zircaloy, 35 day Nb-95 interference
Sr-90	5.91% fission yield	0.04	Interference from 50.5 day Sr-89
Tc-99	6.12% fission yield	0.3	
I-129	0.74% fission yield	0.008	Interference from 8.04 day I-131
Cs-135	6.54% fission yield	84	Cs-135:Cs-137 Fission Activity 1.1×10^{-5}:1 10 CFR 61 limits 84:1 Also, 2.06 yr Cs-134 interference
Cs-137	6.22% fission yield	1.0	

5) I-129 and Te-99 should be correlated to readily measured fission products having similar transport characteristics.

6) Cs-135 should be eliminated from analysis requirement as it is totally insignificant relative to Cs-137.

7) The alpha emitting transuranics are best estimated by correlations. Pu-241 can be determined by the utilities.

It is obvious that 10 CFR 61 as proposed will have both operational and administrative impacts on light water reactor operation. It also appears obvious that burial costs will successively increase from Class A, to Class B, to Class C wastes. Thus, there is likely to be a severe economic penalty for overclassifying wastes. Moreover, there will be a maximum permissible disposal site inventory for certain nuclides. Overstatement of the concentrations or total quantities of these nuclides could result in premature closing of a burial site. Many of the listed nuclides cannot be analyzed at the power plants. Thus, there will be significant costs for outside analyses required to establish and maintain correlations with more readily measured nuclides. The emphasis on specific activity rather than total package activity may negate the economic advantage of volume reduction as concentrating the waste may result in a more restrictive solid waste classification.

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