

**Using Process Knowledge to Manage Disposal Classification of
Ion-Exchange Resin – 13566**

Jonathan N. Bohnsack, David W. James
DW James Consulting, LLC
855 Village Center Drive #330
North Oaks, MN 55127
jbohnsack@dwjames.com
djames@dwjames.com

INTRODUCTION

It has been previously shown by EPRI [1] that Class B and C resins represent a small portion by volume of the overall generation of radioactively contaminated resins. In fact, if all of the resins were taken together the overall classification would meet Class A disposal requirements. Lowering the classification of the ion exchange resins as they are presented for disposal provides a path for minimizing the amount of waste stored. Currently there are commercial options for blending wastes from various generators for Class A disposal in development. The NRC may have by this time introduced changes and clarifications to the Branch Technical Position (BTP) on Concentration Averaging and Encapsulation [2] that may ultimately add more flexibility to what can be done at the plant level. The BTP has always maintained that mixtures of resins that are combined for ALARA purposes or operational efficiency can be classified on the basis of the mixture. This is a point often misinterpreted and misapplied.

This paper will address options that can be exercised by the generator that can limit B and C waste generation by more rigorous tracking of generation and taking advantage of the normal mix of wastes. This can be achieved through the monitoring of reactor coolant chemistry data and coupled with our knowledge of radionuclide production mechanisms. This knowledge can be used to determine the overall accumulation of activity in ion-exchange resins and provides a “real-time” waste classification determination of the resin and thereby provide a mechanism to reduce the production of waste that exceeds class A limits. It should be noted that this alternative approach, although rarely used in a nuclear power plant setting, is acknowledged in the original BTP on classification [3] as a viable option for determining radionuclide inventories for classification of waste. Also included is a discussion of an examination performed at the Byron plant to estimate radionuclide content in the final waste stream from upstream sampling of reactor coolant and fuel pool water.

NRC Position

Current BTP [4] – For radioactively contaminated ion exchange resins, there is a general rule that various batches of waste combined for classification that the concentrations of classification controlling radionuclides be within a factor of 10 above or below the average concentration of that radionuclide. Recognizing that many plants do not have the capability to differentiate resin streams to that level, the NRC allowed that for where streams were combined for operational efficiency or to minimize exposure to plant personnel the resin can be classified on the basis of the homogeneous mixture.

Proposed Revisions to the BTP [2] – The proposed revisions recognize that whether or not the resins are blended or combined at the point of generation, they may be sent elsewhere for blending with waste from other generators. The revision changes the basis of limiting blending to preclude the mixing of wastes for classification. On one level or another, the BTP was always about blending wastes to manage classification.

USING PROCESS KNOWLEDGE

The original BTP on classification [3] allowed the use of process knowledge as an alternative method for assessing radionuclide inventories for classification. This alternative, while rarely used in a power plant setting, is still a viable option.

Tracking Radioactivity in Resin Waste Streams based on Reactor Coolant Concentrations

All radionuclides are generated in the reactor core and are first seen in the reactor coolant. There are three basic processes for radionuclide release from reactor fuel including direct release of energetic fission products from near surface reactions (recoil), indirect release of fission products that are collided by other energetic particles (knockout), and diffusion from deeper in the fuel matrix (diffusion). The relative importance of these processes depends on the size and extent of defects in the fuel and the amount of fuel contamination on core surfaces. If the fuel is without defects, the fuel contamination or exposed fuel dominates the production of radionuclides seen in the reactor coolant. Small defects (pinhole leaks) allow the release of nuclides that diffuse from the fuel and within the cladding gap but preclude the release of less diffusing radionuclides such as strontium or plutonium isotopes. For these radionuclides, release is mainly limited to that coming from fuel in direct contact with the coolant. In any case, radionuclides observed daily in the reactor coolant can be used to determine the extent to which these release mechanisms are active and extrapolated to determine the release rates of long lived radionuclides important to classification. These determinations are made on the basis of radionuclides with identical chemical and physical properties but with varying half-lives. Most commonly used are the five iodine isotopes (I-131 through I-135). The relative ratios of those with longer half-lives to those with shorter half-lives provide a key to the release pathways and ultimately the release rates of those radionuclides important to classification.

The technology for this process has been long used to track fuel performance to identify the presence of defects. Its application to radioactive waste characterization has been explored but has not been brought into the mainstream. In the early 1990s, when a number of regional disposal sites were under consideration the 3R-STAT computer program developed by Jene Vance [5] was used to do life of disposal site inventory assessments for Tc-99 and I-129. The algorithms supporting this process are equally effective for other radionuclides including Sr-90 and transuranics.

Non-Fuel Source Isotopes

Difficult to measure isotopes not sourced from the fuel require somewhat different treatment. One of the more important of these currently is Ni-63 particularly in PWRs. Ni-63 is formed from the activation of non-radioactive Ni-62. Elemental nickel appears in coolant as a corrosion product from materials in contact with the reactor coolant. Ni-62 is in proportion with other non-radioactive nickel isotopes on the basis of their natural abundance. Given that Ni-63 is difficult to measure, the relative coolant concentration of Ni-63 can be determined through the use of a surrogate, easy to measure radionuclide such as Co-58. Co-58 is primarily an activation product (n,p) of Ni-58. Ni-58 is roughly 20 times more abundant in elemental nickel than Ni-62.

Tracking the Transport

Once the production rates of radionuclides are established, these can be distributed through the three primary release pathways including off gas system, liquid discharge, and solid waste. Significant transfer of iodine radionuclides occurs through steam carry over in BWRs. This carry over accounts for some accrual in condensate resins but most of it is carried to the off gas system through the main condenser air ejector. There is no comparable transfer in PWRs. What remains in the coolant is collected first on ion-exchange resins in the reactor water cleanup on BWRs or CVCS letdown systems in PWRs. In PWRs, in particular, there are a number of processing systems that can be accessed directly or indirectly with reactor coolant. How these systems are operated and duration of operation fixes how much activity will be contained in the resins. In composite they should account for the entire production of the non volatile radionuclides with exception of a relatively small amount of radionuclides in particulates collected in mechanical filters. About 80% of all of the activity should be collected on primary resins (CVCS letdown or equivalent).

Class Controlling Radionuclides (Problems and Considerations)

Radioactive resin classification at the Class A level is most frequently dominated by a narrow range of isotopes. Recent experience has shown Ni-63 becoming increasingly important in classification. This appears to be driven by aging of the contamination layer in the operating plants and various efforts to reduce contamination for ALARA consideration. These efforts include Zinc injection to displace Co-60 by replacing it with the shorter half-life and less toxic Zn-65. In addition, pre-outage system forced oxidation with hydrogen peroxide (H₂O₂) oxidizes the

crud layer from the surface and pulls out metal ions (including cobalt and nickel) oxidized in the process. As Co-60 decays, relative to Ni-63 the scaling factor increases. This effect is most evident in the spent fuel pool. Ni-63 is most problematic in PWRs as a result of the higher dependence on high nickel alloys for fuel cladding and steam generator tubes.

If the plant has a history of fuel failures, cesium 137 will be present accompanied by Sr-90. A fuel failure results in an initial spike in the Cs-137 activity which will persist at an elevated level until the assembly is removed. Since cesium is a gamma emitter it is readily tracked in reactor coolant. Using this information it is possible to estimate the total Cs-137 release and removed by the demineralizer system. This information can be used to manage cesium activities in various streams to isolate problem beds before they are mixed with larger volumes to avoid raising the classification. The Class B limit for Cs-137 is 150 Ci/m³ or 150 times higher than the Class A limit. If your primary bed Cs-137 concentration is much above 2 or 3 Ci/m³ it is not likely that there is sufficient volume of lower activity material to balance the excess cesium.

C-14 seems to be more localized as a problem. Most plants have not been reporting particular problems with C-14. Since C-14 is produced primarily from activation of the reactor coolant it doesn't have strong connections with radionuclides commonly used for scaling. The small (factor of 10) variation between Class A and Class C tends to work to advantage when classification is exceeded the wastes are more likely to be averageable. In any case, the tracking process described here can work with C-14 with coolant and fuel pool concentration baselines.

Limited Sample Case at Byron

At many of the operating plants, sampling of waste lines was an afterthought in the design process. Designs were developed before the introduction of 10CFR61 and for various reasons broad based sampling options were not included. Sampling may be performed on resin storage tank or taken directly from the final waste package. It is widely held that sampling of the final waste package is the most definitive option for sampling and defining the spectrum of radionuclides in the package. Notably, the spent resin storage tank receives resins from a variety of sources and service functions. Individual stream scaling factors can vary by as much as two orders of magnitude. Grab samples from the SRST or from the disposal liners can provide widely divergent results very often significantly overstating (or understating) one ratio or another and effecting classification. Frequently, due to the activity content of the sample, sample sizes are limited to a few milligrams which could match to any of the streams represented in the tank.

At Byron, an alternative approach is being explored. A general premise in this approach is that radioactivity generated in the reactor is dominantly collected in the letdown cleanup system. This is equally true for both fission products and activation products. Previous work has shown that mechanical filters pick up a relatively small portion of this activity while resins still account for a majority of the activity. In this approach reactor coolant data is evaluated to determine the activity content of the resins based on the processing rates and relative removal. Reactor coolant

is an ideal source for determining waste activity content since it is sampled on a daily basis, provides a broad spectrum of activity, is homogeneous, and can be reliably analyzed by radiochemistry laboratories. The following discussions focuses mainly on the tracking to Ni-63 but could be readily applied to other scaled isotopes.

ESTIMATING RELATIVE PRODUCTION OF NI-63 FROM REACTOR COOLANT

The general equation for production of activation products in reactor coolant can be expressed by

$$\frac{\partial A_i}{\partial t} = \lambda_i N_i \sigma_i \varphi - A_i(\beta + \lambda_i)$$

Where:

- A_i = production rate of Nuclide I (Bq/sec)
- λ_i = Decay Constant(sec^{-1})
- N_i = Atomic density (atoms per cm^3)
- σ_i = Absorption Cross section (10^{-24} cm^2)
- φ = Neutron Flux Rate ($\text{n/cm}^2\text{-sec}$)
- β = Reactor Coolant Cleanup Constant(sec^{-1})

Equilibrium time frames for nuclide production are relatively short in contrast to reactor operating periods. Assuming that observed concentrations in reactor coolant reflect equilibrium production conditions, we can rewrite the above equation in equilibrium (i.e. $\frac{\partial A_i}{\partial t} = 0$). Rewriting the equation:

$$A_i = \lambda_i \frac{N_i \sigma_i \varphi}{(\beta + \lambda_i)} \text{ at Equilibrium}$$

Since the pathways for source material and neutron flux rates are common for most corrosion products it is possible to examine radionuclide ratios with relative proportions of parent isotopes. The Byron reactor coolant chemistry data was examined for the presence of activation products common to reactor and steam generator structural materials. These are summarized along with critical properties in Table 1 below.

Table 1: Nuclide Properties

Nuclide	Fe59	Co58	Cr51	Co60	Ni63
Half-life (days) [6]	44.63	70.8	27	1924.868	36561.53
Half-life (Seconds)	6.427E+05	1.020E+06	3.888E+05	2.772E+07	5.265E+08
Decay Constant (sec-1)	1.079E-06	6.799E-07	1.783E-06	2.501E-08	1.317E-09

Parent Nuclide	Fe58	Ni58	Cr50	Co59	Ni62
Isotopic Abundance [6]	0.0031	0.6727	0.0431	1.0000	0.0366
Reaction	n, γ	n,p	n, γ	n, γ	n, γ
sigma (barns) BWR [7]	0.1264	0.01707	1.521	2.306	1.358
sigma (barns) PWR [7]	0.1223	0.02097	1.473	2.229	1.316
Beta (Cleanup Removal)	1.00E-04	1.00E-04	1.00E-04	1.00E-04	1.00E-04
(lambda + beta)	1.01E-04	1.01E-04	1.02E-04	1.00E-04	1.00E-04

In the PWR primary, inconel is used for steam generator tubes as well as fuel assembly parts and some control components. Given the large area of the steam generator tubes, tube erosion provides the primary supply of nickel and cobalt into the reactor core making inconel the dominant material for production Ni-63 and Co-60. The primary components of Inconel 600 are nickel at 72%, chromium at 15.5%, and iron at 8%. Cobalt tends to most closely follow the nickel concentrations and can run from 4000-12000 ppm. It is assumed that the ratios in the reactor coolant are close to the production ratios. This is because the cleanup removal rate is high relative to the decay removal rate. Even with Co-58 half-life of 70 days the cleanup half-life is not more than 2 or 3 days. Assuming that the elemental cobalt concentration is nominally 4500 ppm and basing on the above assumptions the estimated reactor coolant ratios with Co-60 are listed in Table 2 below:

Table 2: Estimated Reactor Coolant Ratios

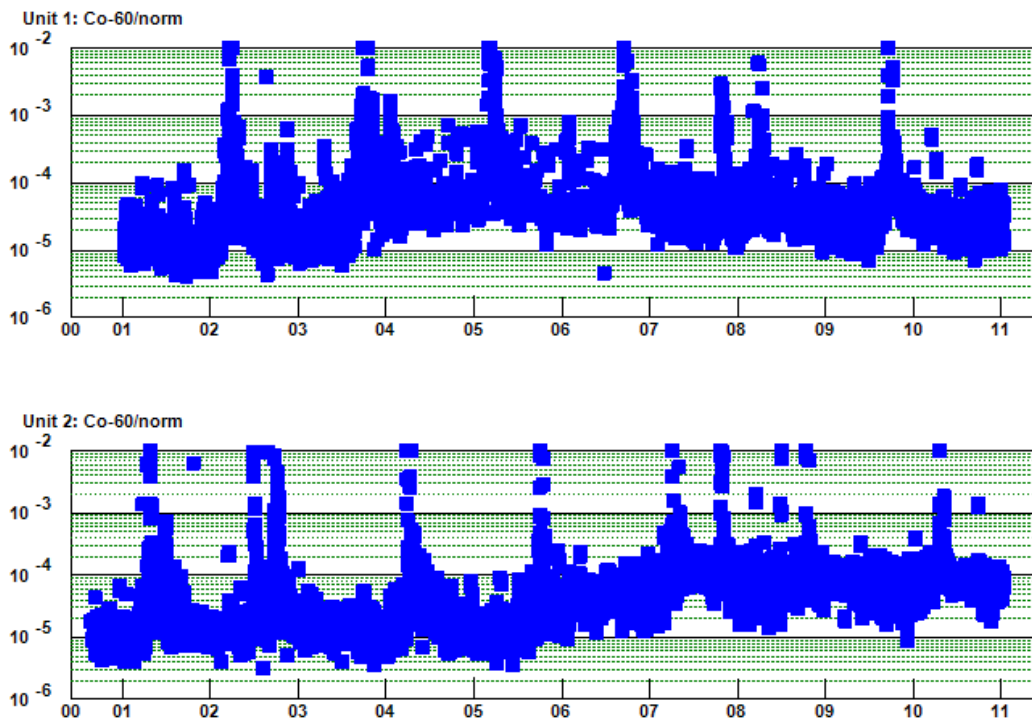
Nuclide Ratio	Fe-59/Co-60	Co-58/Co60	Cr-51/Co-60
Predicted Ratio	0.12	26.05	2.79
U1 10/19/03-016-07– observed Ratio	1.15	25.64	7.87
U1 Predicted/observed	9.17	0.98	2.82
U1 3/14/05-4/2/08– observed Ratio	1.95	35.2	9.7
U1 Predicted / Observed	15.61	1.35	3.47
U2 3/31/07-8/4/08– observed Ratio	0.36	28.7	2.66

U2 Predicted/observed	2.88	1.10	0.95
U2 5/6/10-5/20/11– observed Ratio	0.48	26.73	3.09
U2 Predicted/observed	3.82	1.03	1.11

Based on the observations, Co-58 most closely matches the predictions. In addition, Co-58 is an activation production of a nickel isotope. Drawing on this result it is assumed from the result from Co-58 comparisons that the relative concentrations of elemental nickel and cobalt in the primary coolant the process are as represented. Extending the prediction, the Ni-63/Co-60 reactor coolant ratio is estimated to be ~ 0.18. This is consistent with ratios estimated from production codes assuming elemental distributions consistent with high nickel alloys.

Sampling experience has been impacted by zinc injection along with efforts to reduce the contamination layers in the primary. Zinc injection acts to displace the cobalt in the surface layers and mobilize it through the CVCS cleanup system. This long term by finite impact is observed in Figure 1 showing the elevated cobalt activity in the Byron Unit 2 reactor coolant.

Figure 1 Reactor Coolant Tracking of Co-60 Concentration



Zinc injection was started in Unit 2, following the refueling outage in 2005, Co-60 remains elevated, perhaps, around a factor of 5 higher than pre-injection levels. Effectively the

production rates for Co-60 have not significantly changed. What has remained changed is that the Co-60 that is produced is mostly mobile and available for removal. Intuitively, if the cobalt is targeted for mobilization, the expectation would be that ratios in reactor coolant between Ni-63 and Co-60 in resins and filters would be reduced. Since this is not the case based on waste sample records, the indication is that nickel is as strongly (or more strongly) mobilized as cobalt. Higher ratios could reflect the aging of the crud layer where Co-60 has decayed proportionately more than Ni-63. Expected ratios assuming constant removal and minimum transport delay would be on the order of 0.1. Assuming that the contamination layer has been aged by nominally half of the plant life, the Ni-63/Co-60 would be about 8 times the un-delayed ratio. It's expected that a higher ratio would tend to be more dominant during the pre-shutdown shock of the system. During normal operation it would be expected that the ratios in reactor coolant and corresponding ratios in the CVCS beds would correspond to the steady state production ratios.

USING REACTOR COOLANT DATA PROVIDE CONTINUOUS INVENTORY

Since the SRST at Byron was cleared in 2008, a record of transfers to the tank has been maintained by plant personnel. Using this information along with reactor coolant activity concentrations, we can explicitly track the inventory in the spent resin tank. Primary beds containing lithiated mixed beds run for two cycles and are sidelined during outages. The shutdown beds containing normal mixed beds are brought on line just before the outage to receive the initial crud burst initiated with the H₂O₂ injection. These beds interact directly with reactor coolant and see no prior processing. In each comparison the relative activity collected in the shutdown bed was comparable in scale to that collected in the operating beds. In any case the corrosion products mobilized by the peroxide injection are reflected in the measured coolant concentrations. Using the same removal parameters we can get an estimate of the overall activity removed.

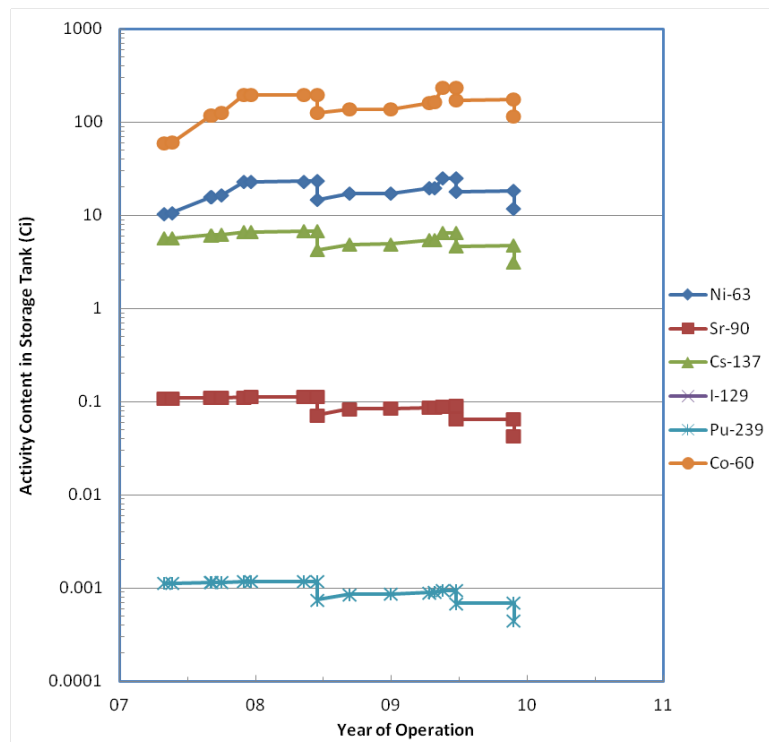
Iodine ratios in the reactor coolant data provide a mechanism to predict the generation of fission products and transuranics. Activation products including Co-58, Co-60, and Mo-99 can provide a basis for determining the generation of nickel 63 and activation generated Tc-99. In this case the algorithms from 3R-STAT [5] are used to determine fission products. Ni-63 can be tracked by its relation with Co-58. Since both are activation products of elemental nickel, there is a common and reliable origin. Results from this correlation are benchmarked with Co-60 generation records to calibrate the actual generation.

The accumulation of activity in any given resin bed is dependent on the incoming concentration of the element in the stream. It is also dependent on the effective removal factor that can be attributed to the resins. Often if one applies the concentration observed in the reactor coolant and assumes a high decontamination factor, the estimated accumulation is exorbitant. A better fix can be made by relating removal to historical disposal records of cobalt 60.

Prior to the transfer of a batch of high activity resins, reactor coolant data is examined to estimate the total activity carried by the batch. The operator determines whether or not the batch can be accommodated in the resin storage tank. That is whether the activity carried in the resin receiver tank can be averaged to disposal requirements when the new batch is added. Accumulation of activity in each ion exchanger can be monitored through its entire cycle to verify that the best choices are made with respect to its disposition.

In the case examined here, what is observed is that it is possible to predict activity content in the ion exchanger beds before they are discharged to the storage tank. Figure 2 shows the accumulation of activity in the resin storage tank along with activity removals as liners are filled during the processing. As each new bed is added the activity in the tank is decayed from the last entry up to the date of the new one to assure that the inventory is constantly current. In this example there were three liners filled during the period following rebase lining of the tank.

Figure 2: Monitoring Critical Nuclide Activity in the Spent Resin Tank



The balancing process doesn't specifically need to start with an empty tank. A best estimate can be constructed of the tank activity breakdown and determine the ultimate disposability within the context of anticipated activity generation.

Figure 3: Tracking Concentration (Another Perspective)

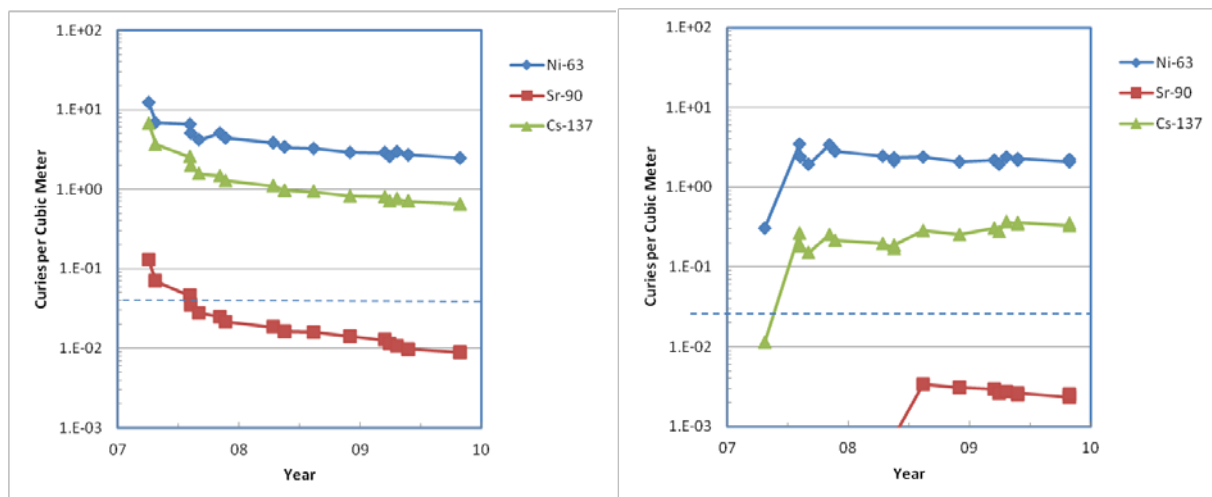


Figure 3 provides another perspective on the activity tracking. Basically a real time volume based concentration can be developed for critical radionuclides staged for disposal. In the example case here, the hottest batch was added to tank first (left plot). The impact of this was to pull all of the subsequently added batches into a higher disposal classification. The right plot in Figure 3 shows that effectively all three of the liners pulled could have met Class A disposal requirements if the first batch was redirected or processed out immediately.

SAMPLE ANALYSIS PROGRAM IMPLEMENTATION (SCAN5-3R)

The methodology developed by Vance & Associates has been incorporated into the DW James SCAN computer code [8] to augment the analysis of reactor coolant data for the purpose of estimating the release rates of radionuclides important to disposal classification. Samples collected on a daily basis are input into the SCAN program through direct download from the Reactor Coolant Chemistry database. A series of calculations are performed to determine release rates of fission products and transuranic radionuclides based on the five iodine isotopes typically found in reactor coolant. Based on the ratios the amount of activity released from fuel defects can be differentiated from activity released from fuel contamination. Results are recorded for each day's sample and made available for trending and integration of the activity released. A typical sample output is presented in Table 3;

Table 3: Sample SCAN5-3R Output

Isotope Activities (μCi/ml)			
I-131	1.70E-04	I-132	4.43E-03
I-133	2.34E-03	I-134	6.76E-03
I-135	4.88E-03		
Cs-134	2.17E-05	Cs-137	1.75E-05
Co-60	3.42E-05		
Reactor % Power	1.00E+02	Letdown Flow	8.00E+01

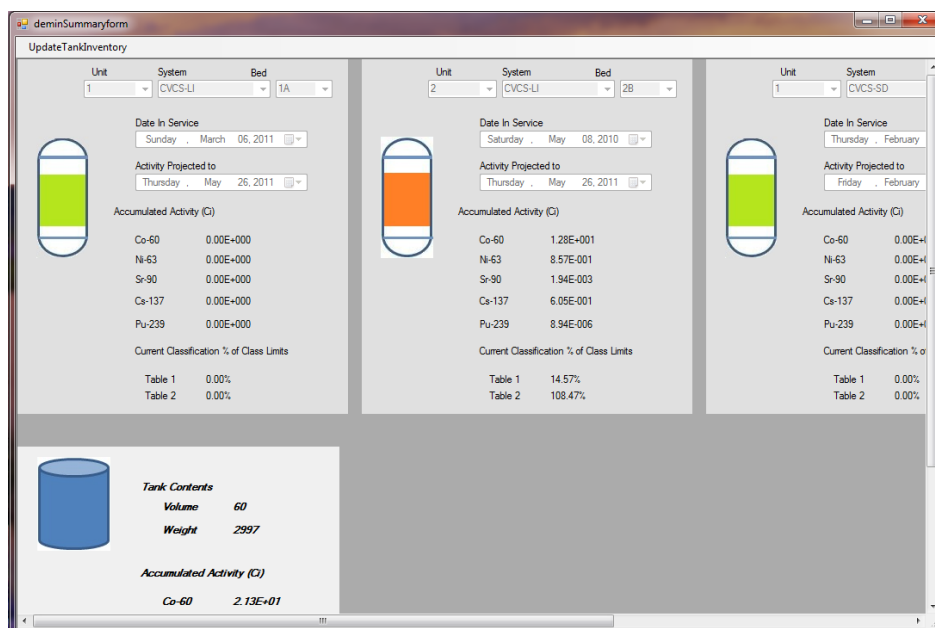
Analysis Results:

Escape Rate Coefficient	9.12E-04	Exposed Fuel Fraction	9.95E-01
Defective Fuel Fraction	5.00E-03	Recoil Fraction	9.00E-01
Diffusion Fraction	3.00E-02	Knockout Fraction	7.00E-02
Convergence	1.70E-01		
Defective Fuel Age	6.97E+02		
	Inst.Release Rate	Daily Release	Coolant Conc
Nuclide	(μCi/sec)	(Ci/Day)	(μCi/cc)
I-129	6.43E-10	5.56E-11	1.42E-13
Tc-99	2.51E-07	2.17E-08	5.52E-11
Sr-90	1.45E-03	1.25E-04	3.19E-07
Pu-239	2.40E-06	2.07E-07	5.27E-10
	Analysis Check		
Using Cs-137:	Measured	Calculated-ANS	Calculated-RSS
Cs-137(μCi/sec)	1.47E-02	1.92E-03	2.06E-03

Concentrations of critical isotopes including I-129, Tc-99, Cs-137, Sr-90, and Pu-239 are estimated in reactor coolant along with daily release rates based on relative cleanup coefficients determined from reactor volume and cleanup/letdown flow rates. Additional internal calculations are performed to estimate Ni-63 release rates from neighboring isotopes and the activation contribution to Tc-99 from measured Mo-99. The methodologies for these determinations were pioneered by Jene Vance and are the subject of an approved NRC topical report. [5]

Based on the daily release rates, assuming equilibrium conditions, it's a relatively simple extrapolation to track the activity buildup in the online primary coolant demineralizers. Second tier demineralizer activities which account for a small portion of the activity release overall can be related to the primary coolant demineralizers. Once the tracking is established the user can follow activity collection in the plants demineralizers to monitor waste classification in the demineralizers and determine the disposition of the demineralizers as an informed process. The SCAN5 3R program includes a user interface which allows the user to view the current activity loading and classification of the each demineralizer followed. This interface can also be used to manage waste classification. It allows the user to take advantage of the extensive sampling and monitoring that is performed at the plant with greater confidence and understanding of the waste streams and interpreting sample data that may be collected. Figure 4 below provides a partial view to the interface dialog. Demineralizers are color coded to show their current status, the vessel is shown in green while the estimated disposal class is less than 80% of the Class A limit, orange signifies less than 120% of the Class A limit which would likely be still averageable.

Figure 4: SCAN5-3R Demineralizer Status Window



The program user can test the impact of moving any individual bed into resin mixing tank and know in advance how the resulting mixture will be impacted. Again this allows the user to make informed decisions to manage the disposition of material collected through this process.

CONCLUSION

Direct sampling of waste for the basis of characterization and classification has its limitations. The small sample size relative to the total waste volume inherently makes obtaining a truly “representative” sample difficult. However, if the sample results are all that is available to go on, one is constrained to apply them conservatively since there is no way to corroborate the findings. Dipping into the SRST or a waste liner for a sample is like Forest Gump’s box of chocolates. It does little to reveal the entire contents of the tank. Even with a sample history, one is limited if it is not possible to ascribe particular ratios to individual sources and account for total contributions by stream. With the use of coolant history data you have an on-going assessment of activity production in the plant by its presence in reactor coolant. This can be extrapolated to waste streams through mass and activity balance processes to create reliable and defensible bases for disposal. In the process you can take advantage of the extensive sampling already performed, have a better handle on your resin wastes, save on operator exposure, and likely have significant cost savings as well.

ACKNOWLEDGEMENTS

Miguel Azar, Exelon Corp.
Lilit Michigan, Drew Kolste, Exelon Byron
Eric Cieszkiewicz, Exelon Braidwood
Clint Miller, PG&E, Diablo Canyon

REFERENCES

- [1] Electrical Power Research Institute, *An Evaluation of Alternative Classification Methods for Routine Low Level Waste from the Nuclear Power Industry*, 2007.
- [2] U.S. Nuclear Regulatory Commission, *Draft Branch Technical Position on Concentration Averaging and Encapsulation Rev. 1*, 2012.
- [3] U.S. Nuclear Regulatory Commission, *Branch Technical Position on Waste Classification*, 1983.
- [4] U.S. Nuclear Regulatory Commission, *Branch Technical Position on Concentration Averaging and Encapsulation*, 1995.
- [5] Vance and Associates, *3R-STAT Topical Report*, 1994.
- [6] U.S. Department of Energy, *Chart of the Nuclides*, 2002.
- [7] Oak Ridge National Laboratory, *ORIGEN 2.1 - Isotope Generation and Depletion Code, Matrix Exponential Method*.
- [8] DW James Consulting, *SCAN4 Technical Report*, 2012.