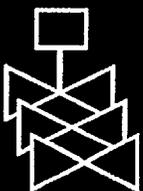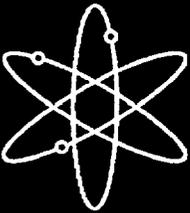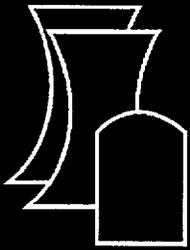# Low-Level Radioactive Waste Classification, Characterization, and Assessment: Waste Streams and Neutron-Activated Metals

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Low-Level Radioactive Waste Classification, Characterization, and Assessment: Waste Streams and Neutron-Activated Metals

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Abstract

This study was conducted to provide NRC, other federal and state regulatory agencies, nuclear utilities, and low-level radioactive waste (LLW) managers with further information on radionuclide source terms that will improve the health and safety aspects of LLW management and disposal. The goal of this work was to enhance the understanding of the occurrence, distribution, and assessment of the radiological impacts of radionuclides associated with neutron-activated metals and other LLW streams from commercial nuclear power stations. This study focused on identifying and characterizing a group of very long-lived radionuclides that are not specified in 10 CFR Part 61, but which are present in significant concentrations in various types of LLW materials generated at commercial nuclear power stations. The concentrations of ^{10}Be, ^{36}Cl, ^{93}Mo, ^{93m}Nb, ^{108m}Ag, ^{113m}Cd, and ^{121m}Sn (as well as the specified 10 CFR Part 61 radionuclides) have been measured in a variety of neutron-activated metal and spent primary demineralization resin LLW samples obtained from U. S. nuclear power stations. This work required the development of new or modified radiochemical separation, purification, and counting procedures to measure these radionuclides in the LLW materials of interest. Of this group of radionuclides, the ^{10}Be, ^{36}Cl, and ^{108m}Ag appear to be present in some types of LLW materials in sufficient quantities to warrant further investigations to better assess their radiological and environmental impacts associated with LLW disposal. It is recommended that further studies be focused on: 1) providing an accurate assessment of the total quantities of these radionuclides in LLW from these sources, 2) determine the leaching characteristics of these LLW materials, 3) determine the migration behavior and environmental pathways of these radionuclides upon release from LLW disposal facilities, and 4) provide performance assessment modelers with the necessary radiological/geochemical information to better predict the potential impacts from disposal of this group of radionuclides. Activity scaling factors

have been developed for all of the additional radionuclides measured in this study. The use of activity scaling factors for estimating the concentration of a radionuclide in LLW is permitted by 10 CFR Part 61.55, and this method is desirable for radionuclides such as those listed above that are difficult to measure directly in LLW materials. Consistent scaling factors for a wide variety of LLW materials were determined for ^{93}Mo and ^{93m}Nb relative to ^{60}Co over a concentration range of four orders of magnitude. Generic scaling factors for the other long-lived radionuclides measured in this study showed much greater variability due to the unique composition of some of the materials. However, in some cases useful scaling factors were obtained when similiar LLW materials were considered as a group. In addition to these radionuclides, an assessment was conducted to provide an updated understanding of the occurrence, distribution, and activity scaling factors of ^{14}C, ^{99}Tc, and ^{129}I, as well as an evaluation of the ^{59}Ni/^{63}Ni activity ratio in LLW. This assessment has shown that the concentrations and associated activity scaling factors of ^{99}Tc and ^{129}I are several orders of magnitude lower than values published earlier in nuclear power industry data bases, thereby significantly reducing the radiological/environmental impacts associated with their disposal in LLW. The assessment of the ^{59}Ni/^{63}Ni activity ratio in LLW indicated that early reported values of this ratio were too high by up to factors of 5-10. This was probably due to systematic and/or random uncertainties in their radiochemical analyses. More recent analyses and assessments indicate that this ratio should range from about 0.006 to 0.012, depending upon the neutron flux and irradiation time. Activity scaling factors for ^{10}Be, ^{36}Cl, ^{93}Mo, ^{93m}Nb, ^{108m}Ag, ^{113m}Cd, and ^{121m}Sn relative to ^{60}Co were determined for a variety of activated metal and LLW samples. These scaling factors are believed to be the first published in the literature for these radionuclides.

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Executive Summary

The technical requirements for land disposal of low-level radioactive waste (LLW), as specified in 10 CFR Part 61, necessitates that specific waste classification and characterization be performed on LLW before disposal. Waste classification involves the quantification of specified radionuclides in the waste materials to comply with disposal requirements and disposal site performance objectives. With the aging of commercial nuclear power stations, increasing quantities of neutron-activated metal LLW are being generated as replacement of hardware components within the reactor pressure vessel becomes necessary. In addition, relatively large amounts of spent ion exchange resins used for cleanup of reactor coolant water and other aqueous waste streams are being generated for disposal.

The research work conducted in this project has addressed key issues associated with the characterization and disposal of all long-lived radionuclides of potential concern in neutron-activated metal wastes and other related waste streams. The objectives of this research were: 1) to identify all long-lived (half-lives greater than five years) activation products of potential concern (in addition to those specifically listed in 10 CFR Part 61) that may be present in various types of LLW in significant amounts, 2) to develop new or revised radioanalytical procedures for the measurement of the additional long-lived radionuclides of interest, 3) to enhance NRC's understanding of the distribution and projected quantities of additional long-lived radionuclides in neutron-activated metal wastes and other related waste streams from commercial nuclear power stations, 4) to determine appropriate activity scaling factors for the difficult-to-measure radionuclides for use when the sample results are near or below the lower-limit-of-detection, and 5) to provide an assessment of the radiological and environmental impact of those additional radionuclides not specified in 10 CFR Part 61.

Since the enactment of 10 CFR Part 61, other long-lived radionuclides have been identified (e.g., ^{10}Be, ^{36}Cl, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, and ^{121m}Sn) which are not routinely measured, but which potentially may be of concern in certain types of LLW. These radionuclides are primarily associated with neutron-activated metal wastes (e.g., spent control rod assemblies and reactor internal components) and other types of LLW (e.g., spent ion exchange cleanup resins) being generated by the nuclear power industry for disposal at shallow-land LLW burial grounds.

Of the group of additional radionuclides measured in this project, ^{10}Be, ^{36}Cl, and ^{108m}Ag appear to have the greatest potential impact with respect to 10 CFR Part 61. Although none of these radionuclides were present in the LLW examined in this study in quantities high enough to seriously impact the current LLW classification and shallow-land disposal criteria specified in 10 CFR Part 61, further radiological and environmental assessments may want to be considered to determine if they should be amended to 10 CFR Part 61.

Beryllium-10 is of special interest because of its potential to be produced in relatively large quantities in nuclear power station LLW, originating in spent BWR and PWR control rods and in spent primary coolant demineralization resins. The ^{10}Be is produced by neutron activation of ^{10}B present as neutron absorbing materials, boron carbide and borosilicate glass in control rods, and as soluble borate added to PWR reactor coolant. The extremely long half-life of ^{10}Be (1.6E6 years), together with a relatively high ingestion dose conversion factor and a relatively low Kd value for adsorption onto sandy types of soil, create the potential for long-term migration and offsite radiation exposure of this radionuclide from LLW disposal facilities. This study has shown that ^{10}Be could be the third most abundant radionuclide in spent control rods and in some PWR spent primary resins after a decay time of about 600 years. Therefore, it is recommended that further studies be conducted to: 1) provide an accurate assessment of the total quantities of ^{10}Be contained in LLW from these sources, 2) determine the ^{10}Be leaching characteristics from LLW, 3) determine the migration behavior and environmental pathways of ^{10}Be released from LLW disposal facilities, and 4) provide performance assessment modelers with the necessary radiological/geochemical information to evaluate the potential impacts from disposal of this radionuclide in LLW.

Silver-108m is also of interest because of its production in large quantities in PWR spent RCCA control rods which contain 80% silver. Silver-108m has a 130 year half-life and a relatively high ingestion dose conversion factor due to its multiple high-energy gamma-ray emissions. Silver-108m will easily be the most abundant radionuclide in spent RCCA control rods for many hundreds of years. It is therefore of some concern from a waste disposal perspective. Fortunately, the stable metallic waste form and the expected high soil Kd values should minimize the leaching rate and offsite transport of this radionuclide during water infiltration at a LLW disposal facility. Nevertheless, it is recommended that further studies be conducted for ^{108m}Ag, as described in the above paragraph for ^{10}Be, to better understand the radiological, environmental, and health impacts associated with the disposal of neutron-activated metal components containing ^{108m}Ag.

Chlorine-36 is the other very long-lived radionuclide measured in this study that deserves further assessment from a LLW disposal standpoint. Its very long half-life (3.01E5 years), relatively high ingestion dose conversion factor, and high environmental mobility combine to create the potential for long-term migration from a LLW disposal facility. Fortunately, the concentrations of ^{36}Cl in LLW from commercial nuclear power stations are quite low. Chlorine-36 is produced almost exclusively in nuclear power plants by neutron activation of soluble chloride impurities present in the reactor coolant water, and is then concentrated on primary demineralization resins used for reactor coolant cleanup. Because chloride ions accelerate the corrosion of stainless steel in the reactor primary loop, great care is taken to minimize the chloride concentrations in reactor coolant water, and typical concentrations are in the low ppb range. This is sufficient to produce about 0.0001 to 0.002 uCi/g of ^{36}Cl in spent primary resins. This equates to an estimated 0.2 to 5 Ci/y of ^{36}Cl in primary resin LLW from all PWR nuclear power stations in the U. S. As discussed in Section 6.1 of this report, LLW disposal site performance assessment modeling, using a source term containing only 0.1 Ci of ^{36}Cl was sufficient to predict that this radionuclide would be the major

contributor to the offsite radiation dose for the contaminated well/drinking water exposure scenario. Because of this potential for radiation exposure, it is recommended that further studies similar to those described in the above paragraph for ^{10}Be be conducted to obtain a better understanding of the radiological and environmental impacts from disposal of this radionuclide in LLW.

The other additional radionuclides measured in this study, ^{93}Mo, ^{113m}Cd, and ^{121m}Sn, either have half-lives that are too short to be of consequence in LLW disposal, or in the case of ^{93}Mo, the concentrations do not appear to be high enough to contribute significantly to the potential radiation exposure.

Activity scaling factors have been developed for all of the additional radionuclides measured in this study. The use of activity scaling factors for estimating the concentration of a radionuclide in LLW is permitted by 10 CFR Part 61.55, and this method is desirable for radionuclides such as those listed above that are difficult to measure directly in LLW materials. Consistent scaling factors for a wide variety of LLW materials were determined for ^{93}Mo and ^{93m}Nb relative to ^{60}Co over a concentration range of four orders of magnitude. Generic scaling factors for the other long-lived radionuclides measured in this study showed much greater variability due to the unique composition of some of the materials. However, in some cases useful scaling factors were obtained when similiar LLW materials were considered as a group.

Recent measurements and assessments of ^{129}I and ^{99}Tc in LLW from commercial nuclear power stations have shown that the true concentrations of these radionuclides are several orders of magnitude lower than previously reported values. Very sensitive mass spectrometric analytical methods were utilized to determine the concentrations and activity scaling factors for ^{129}I and ^{99}Tc in a wide variety of LLW samples from a number of PWR and BWR stations in the U. S. (Robertson, et al., 1997). These measurements provided concentrations and associated activity scaling factors (relative to ^{137}Cs and ^{60}Co) for these radionuclides that were two to four orders of magnitude lower than the very conservative values published in

several nuclear power industry data bases. Geometric mean values of the $^{129}I/^{137}Cs$ scaling factor for LLW from PWR and BWR stations measured in this study were 6.48×10^{-8} and 4.25×10^{-7}, respectively. The geometric means for $^{99}Tc/^{137}Cs$ in LLW from PWR and BWR stations were 7.37×10^{-7} and 3.21×10^{4}, respectively. The correlations between ^{99}Tc and ^{60}Co were considerably better than the correlations between ^{99}Tc and ^{137}Cs, and the geometric mean values of the $^{99}Tc/^{60}Co$ ratios for PWR and BWR stations were 1.70×10^{-6} and 1.18×10^{6}, respectively.

Because performance assessment modeling studies of LLW disposal facilities have indicated that ^{129}I and ^{99}Tc (as well as ^{14}C) will be the limiting radionuclides with regard to the total quantities of LLW permitted at a site, it is important to determine as accurately as possible the actual quantities of these radionuclides being disposed in LLW. The mass spectrometric measurements performed during this study have clearly shown that when the true concentrations and activity scaling factors are used for performance assessment modeling, the ^{129}I and ^{99}Tc no longer become limiting radionuclides for LLW inventories at disposal facilities. Disposal facilities will, therefore, be able to accommodate larger quantities of LLW at each facility, thereby minimizing the expense of developing additional disposal sites.

An assessment of the ^{63}Ni and ^{59}Ni production and activity scaling factors in LLW was conducted to evaluate the accuracy of past measurements of these radionuclides. This assessment indicated that early reported values of the $^{59}Ni/^{63}Ni$ activity ratio were too high by up to factors of 5 to 10. More recent analyses and assessments indicate that this ratio should range between about 0.006 to 0.012, depending upon the neutron flux and the irradiation time of the exposed materials. In any event, this activity scaling factor does not appear to be a critical parameter with respect to 10 CFR Part 61 waste classification criteria because the ^{63}Ni, rather than ^{59}Ni, will always be the controlling radionuclide of the two nickel radionuclides in LLW classification.

This study required that a large number of radiochemical separation and purification procedures, as well as special radiation detection methods be developed to measure the additional group of radionuclides addressed in this study. Appendix A of this report contains the radiochemical procedures that were developed during this study. Detailed procedures are presented for ^{10}Be, ^{36}Cl, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{93m}Nb, ^{94}Nb, ^{93}Mo, ^{99}Tc, ^{109}Cd, ^{113m}Cd, ^{121}Sn, as well as Pu, Am, and Cm isotopes. Additional radioanalytical information used to help develop the radiochemical procedures given in Appendix A are published in: Thomas, C. W., Thomas, V. W., and Robertson, D. E., "Radioanalytical Technology for 10 CFR Part 61 and Other Selected Radionuclides", NUREG/CR-6230, U. S. Nuclear Regulatory Commission, Washington, D. C., March, 1996.

This study has provided a more comprehensive assessment of the spectrum of long-lived radionuclides that are present in the various types of LLW being generated at commercial nuclear power stations. This work will help insure that the health and safety aspects of LLW disposal are met in a judicious and compliant manner.

Foreword

Increasing amounts of neutron activated metal low-level radioactive wastes (LLW) are being generated at commercial nuclear power stations. Most of these metals are being disposed of as LLW in commercial shallow-land burial facilities. These metals come from a variety of irradiated hardware from the internals of reactor pressure vessels, and this hardware contains a diverse spectrum of radionuclides depending upon the alloy composition. To insure that no unforeseen radiological hazards are associated with the disposal of these materials, a comprehensive examination of neutron-activated metal waste was conducted. In this project a number of long-lived radionuclides heretofore not measured in neutron activated metal wastes have been characterized to determine their occurrence and impacts with respect to 10CFR Part 61 requirements.

These radionuclides include ^{10}Be, ^{36}Cl, ^{93}Mo, ^{93m}Nb, ^{108m}Ag, ^{113m}Cd, and ^{121m}Sn. In addition, this same group of radionuclides, plus ^{99}Tc and ^{129}I and others commonly used for developing activity scaling factors, have also been measured in spent demineralization resins from commercial nuclear power stations. Where appropriate, activity scaling factors for these radionuclides have been developed for specific LLW types to facilitate the rapid estimation of the concentrations of these difficult-to-measure radionuclides. This comprehensive examination and assessment of these additional radionuclides measured in activated metal and spent ion exchange resin LLW has shown that no significant changes to 10CFR Part 61 requirements would be necessary based on their observed radiations, concentrations, inventories, and environmental behaviors.

Acknowledgements

1 Introduction

Since the enactment of the U. S. Nuclear Regulatory Commission (NRC) rule on "Licensing Requirements for Land Disposal of Radioactive Waste", 10 CFR Part 61 (Federal Register 1988), a great deal of experience and information has been developed on the radiological and physical properties and quantities of low-level waste (LLW) being generated and disposed by commercial nuclear power stations. Despite this abundance of information, there are a number of areas where additional data are needed to clarify ambiguities, present more accurate analytical results, and provide a more comprehensive assessment of the requirements of 10 CFR Part 61. This project was initiated to conduct empirical measurements of long-lived radionuclides, particularly those not specified in 10 CFR Part 61, but which could be present in some LLW types, including neutron activated metals, in significant concentrations.

The reasons for conducting these studies include: 1) more neutron-activated metals are being disposed of as LLW, 2) the activated metal LLW is frequently not being adequately analyzed for all long-lived radionuclides, and 3) activated metal wastes are not included in performance assessment modeling of LLW disposal facilities.

The relationship of these additional radionuclides with other 10 CFR Part 61 radionuclides, particularly those gamma-emitting radionuclides used for developing activity scaling factors, would help determine if further radiological, dosimetric, and environmental assessments are warranted. This work includes: 1) a literature assessment of the additional radionuclides [this task has been published as NUREG/CR-6230 (Thomas, Thomas and Robertson, 1996)], 2) the development of radiochemical procedures for their measurement in LLW, 3) determination of their concentrations (as well as the specified

10 CFR Part 61 radionuclides) in a variety of neutron-activated metal wastes and primary coolant cleanup resins, 4) an assessment of the activity scaling factors for the additional radionuclides and several 10 CFR Part 61 radionuclides which need clarification, and 5) an assessment of the relative concentrations of ^{59}Ni and ^{63}Ni in activated metal

waste to provide more accurate estimates of the activity ratio (scaling factor) for these radionuclides, and 6) an assessment of the impact of the additional radionuclides on waste classification and shallow-land disposal of LLW.

1.1 Low-Level Waste Classification and Characterization Requirements of 10 CFR Part 61

The technical requirements for land disposal of LLW, as specified in 10 CFR Part 61, necessitates that specific waste classification and characterization be performed on LLW before disposal. Waste classification involves the quantification of specified radionuclides in the waste materials to comply with disposal requirements and disposal site performance objectives. Since the enactment of 10 CFR Part 61, other long-lived radionuclides have been identified (e.g., ^{10}Be, ^{36}Cl, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, and ^{121m}Sn) which are not routinely measured, but which potentially may be of concern in certain types of LLW. These radionuclides are primarily associated with neutron-activated metal wastes (e.g., spent control rod assemblies and reactor internal components) and perhaps other types of LLW which the nuclear power industry is generating in increasing amounts for disposal at shallow-land LLW burial grounds.

A more comprehensive radionuclide analyses of the various types of neutron-activated metal wastes is therefore warranted to insure that these radionuclides do not pose a problem to public health and safety. In addition, the environmental fate of these long-lived radionuclides once they are disposed at LLW disposal facilities is of further concern. In order to predict the migration of these radionuclides from disposal sites, it is necessary to determine their leaching rates from the various neutron-activated metal matrices by simulated or actual waste trench solutions and/or groundwaters. The chemical forms of the resulting soluble radionuclides species are also important for predicting their movement through soils.

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The concentration of a radionuclide in wastematerials is normally determined by direct measurements or indirect methods, such as the use of activity scaling factors which relate the inferred concentration of a difficult-to-measure radionuclide to another that is easily measured by gamma-ray spectrometry. For a number of radionuclides (e.g., ^{14}C, ^{99}Tc, and ^{129}I), the activity scaling factors used in the nuclear power industry have been overly conservative, since the factors were based primarily on "less-than" values corresponding to the lower-limit-of-detection of the analytical methods used by the commercial analytical service laboratories performing the analyses. This methodology has not generally influenced the classification status of the waste, but does artificially increase the inventories of these radionuclides within waste containers, and subsequently the total inventories of these isotopes at LLW disposal sites.

Recent site performance assessment modeling of proposed LLW disposal sites has indicated that the total disposal site inventories of these radionuclides are often the controlling factors for the total quantities of radioactive waste permitted in a LLW shallow-land burial facility (Vance 1988). Thus, overly conservative estimates of the concentrations of these isotopes in LLW could lead to premature closure of a disposal facility. It is therefore important that waste generators utilize the most accurate scaling factors possible, so that reliable estimates of the total

quantities of these nuclides can be made.

1.2 Project Scope

The research work conducted in this project has addressed key issues associated with the characterization and disposal of all long-lived radionuclides of potential concern in neutron-activated metal wastes and other related waste streams. The objectives of this research were: 1) to identify all long-lived (half-lives greater than five years) activation products of potential concern (in addition to those specifically listed in 10 CFR Part 61) that may be present in various types of LLW in significant amounts, 2) to develop new or revised radioanalytical procedures for the measurement of the additional long-lived radionuclides of interest, 3) to enhance NRC's understanding of the distribution and projected quantities of additional long-lived radionuclides in neutron-activated metal wastes and other related waste streams from commercial nuclear power stations, 4) to determine appropriate activity scaling factors for the difficult-to-measure radionuclides for use when the sample results are near or below the lower-limit-of-detection, and 5) to resolve discrepancies between calculated versus measured concentrations of ^{59}Ni and ^{63}Ni in neutron-activated metal LLW.

2 Radionuclide Production and Distribution in LLW Generated at Nuclear Power Stations

Radionuclides contained in nuclear power station LLW generally originate from four main sources: 1) leakage of fission products from defective fuel or from tramp uranium on the fuel assembly surfaces, 2) neutron activation of metal components contained within the reactor pressure vessel, 3) neutron activation of corrosion products leached from primary loop components and transported by the reactor coolant to the high neutron flux region of the reactor, and 4) neutron activation of impurities in the reactor coolant and activation of the coolant itself. These radionuclides are then redistributed throughout the nuclear power station during demineralization of the primary coolant or the treatment of other liquid waste streams, by spillage of radioactive liquids, and by spreading of solid radioactive corrosion products during station maintenance and component replacement.

The focus of this project has been to examine the radionuclides produced primarily in neutron-activated metal waste components removed from the reactor pressure vessel (e.g., spent control rod assemblies, LPRM hardware, etc.) and performing an analysis/assessment of the long-lived radionuclides not normally measured in these waste components. Of particular interest is the characterization of those long-lived activation products not specified in 10 CFR Part 61, but which may be present in some types of these wastes. Several samples of primary coolant demineralization resins were also included in this characterization since these resins concentrate the fission products and activation products which undergo corrosion and dissolution by the primary coolant.

2.1 Neutron Activation of Materials Inside Reactor Pressure Vessels

This brief discussion pertains primarily to the types of neutron-activated metal wastes that originate within the neutron flux region within the reactor pressure vessel and which must be radiologically characterized before disposal as LLW. These waste types generally consist of expendable or defective reactor components which are replaced during normal reactor operations, and include such items as spent control rod blades and assemblies, spent instrument strings, thimble plug guide tubes, poison curtains, and flow channels. Also, some components associated with spent fuel disassembly hardware generated during fuel rod consolidation projects at nuclear power stations can be treated as LLW. Now that a number of older nuclear power plants have reached decommissioning status, a wide variety of neutron-activated reactor decommissioning wastes are beginning to be generated, including the reactor pressure vessel itself.

A summary of the types, sizes, weights, surface areas, volumes, and materials of construction have previously been summarized and are provided in Tables 2.1 and 2.2 (Bedore, Levin, and Tuite 1987). Much of this radioactive material is close to being Greater-Than-Class-C (GTCC) waste because of its relatively high concentrations of long-lived neutron activation products, and careful radiological characterization of these waste components must be conducted prior to disposal to insure that the Class-C limit is not exceeded.

Table 2.1 Summary of Typical Hardware Characteristics (from Bedore, Levin and Tuite, 1987)

PWR Components	Overall Length (cm)	Configuration	Areal Cross Section (cmxcm)	Weight (kg)	Approx. Volume (cc)	Materials of Construction
Thimble Plug Assemblies	30	Square array of plugs	15X15	5.5	570	304 SS Inconel
Burnable Poison Assemblies	400	Square array of plugs and rods	----	13.6 to 20.4	3700 to 5100	304 SS Inconel Borosilicate
Control Rod Assemblies	400	Square array of plugs and rods	----	74.8	8500	304 SS Inconel Ag/In/Cd
Source Assemblies	400	Square array of plugs and rods	----	13.6 to 16	4300	304 SS Inconel Borosilicate and Source Material
Thimble Plug Guide Tubes	variable	Tubing	1 cm diam.	N/A	N/A	304 SS
BWR Components						
Control Rod Blades	440	Cruciform	25x25	130	18000 (0.018m^3)	304 SS Boron Carbide
Poison Curtains	400	Flat plate	21.0x.2	16.4	1700	Borated SS
Flow Channels	420	Rectangular box	14x14	30	4800	Zircaloy 304 SS
Instrument String	variable	Tubing	1.9 cm diam.	N/A	N/A	304 SS

Table 2.2 Summary of Typical Spent Fuel Disassembly Hardware Characteristics
(from Bedore, Levin and Tuite, 1987)

PWR Components	Overall Length (cm)	Configuration	Areal Cross Section (cmxcm)	Weight (kg)	Approx. Volume (cc)	Materials of Construction
End Fittings	6 to 30	Square	21X21	11.3 to 18.1	1400 to 2250	304 SS
Guide Tubes	variable	Tubing	1 cm diam.	7.5 to 21.2	N/A	Zircaloy
Spacer Grids	7	Square	21.21	4.0 to 12.6	525 to 1660	Inconel Zircaloy
Misc. (Springs, etc.)	----	----	----	0.7 to 11.4	N/A	304 SS Inconel
BWR Components						
End Fittings	17	Square	15x15	5.4 to 15.2	680 to 1900	304 SS
Guide Tubes	variable	Tubing	1 cm diam.	1.7 to 13.2	N/A	Zircaloy
Spacer Grids	4 to 6	Square	15x15	1.1 to 1.6	145 to 210	Inconel Zircaloy
Misc. (Springs, etc.)	----	----	----	0.2 to 1.1	N/A	Inconel

2.1.1 Composition of Reactor Internal Component Construction Materials

The radionuclide composition and quantities generated in neutron-activated metal LLW are directly dependent upon the major and trace element composition of the materials of construction, the neutron fluence, and the decay time after removal from the reactor. The types of construction materials predominantly used in reactor pressure vessel internal components and primary coolant loop materials are generally dominated by stainless steel, with smaller amounts of Inconel and Zircaloy alloys being used in specialized components (Roberts 1981). The elemental compositions of the two types of stainless steel (Types 304 and 316), the five types of Inconel (Types 600, 700, 710, 718, and 750), and the two types of Zircaloy (Types 2 and 4), the most commonly used alloys in nuclear reactor primary systems are given in Table 2.3 for those elements which produce long-lived neutron activation products. Also included is the main type of neutron-absorbing metal alloy (Ag-In-Cd alloy) used in PWR Rod Cluster Control Assemblies (RCCA) control rods. Table 2.3 provides the typical range of concentrations of the parent elements of long-lived neutron activation products that are produced in the types of metal components listed in Tables 2.1 and 2.2.

Although iron and chromium are major constituents in these structural materials, these elements do not produce long-lived neutron activation products, other than ^{55}Fe, a low-energy x-ray emitter with a 2.73-year half-life. Nickel is widely used in stainless steel and Inconel alloys, and produces two long-lived neutron activation products, ^{63}Ni (100 year half-life) and ^{59}Ni (76,000 year half-life).

Great emphasis has been placed on reducing the cobalt content of metal alloys used in nuclear power systems because of the generation of ^{60}Co (5.27 year half-life) and its accompanying high energy gamma radiation. Therefore, cobalt levels in the materials of construction have been in the ppm concentration range, except for several Inconel alloys (Types 718 and 750) which contain 1.0% cobalt to improve hardness.

Niobium is of concern because of the potential for production of ^{94}Nb (2.0E4 year half-life) in alloys containing added niobium. Niobium is present as a trace impurity in ppm concentrations in stainless steels, Zircaloy, and in some Inconels, but it is an additive to Inconel Types 710, 718, and 750, ranging from 1% to 5%.

Molybdenum is also a minor constituent (2-3%) of stainless steel Type 316 and Inconel Types 700 (3%), 710 (2.7%), and 718 (3%). Molybdenum is of concern because it is the parent element of both ^{99}Tc (2.13E5 year half-life) and ^{93}Mo (3500 year half-life), which are environmentally mobile radionuclides.

Tin is a minor additive to Zircaloy Types 2 and 4, being present at 1.2 to 3%, and is also present at 0.3% in Inconel Type 750. Tin can produce ^{121m}Sn (55 year half-life) in these irradiated materials, although the production efficiency is quite low.

Silver, indium, and cadmium are the major neutron-absorbing constituents of PWR Rod Cluster Control Assemblies (RCCA), being present at concentrations of 80, 15, and 5 %, respectively. The silver produces the long-lived ^{108m}Ag (130 year half-life) activation product, and the cadmium produces ^{113m}Cd (14.1 year half-life). There are no long-lived indium activation products.

Chloride impurities in reactor structural materials are purposely kept to an absolute minimum to improve corrosion resistance of the metals. However, it is impossible to eliminate all traces of chloride from these alloys, and stainless steels reportedly have chloride contents ranging from <50 to 130 ppm (Evans, et al. 1984). There is little available information on the chloride contents of the other alloys commonly used in nuclear power

Table 2.3 Summary of Typical Composition Ranges For Metals Used in Reactor Internal Hardware

Element	Stainless Steel		Inconels					Zircaloy-2,4	Ag/In/Cd Alloy
	304	316	600	700	710	718	750		
Fe (%)	68-76	64-65	6-14	7-18	18	18	7	1.5-2.2	<0.002
Cr (%)	18-20	16-18	23	15	---	---	---	0.1	---
Ni (%)	8.0-11	10-14	58-76	52-72	57	53	71	0.02-0.5	0.07-0.12
Co (ppm)	230-2600	1300-1600	400-700	400-700	---	10,000	10,000	10	0.006
N (ppm)	400-1000	300-400	1000-2000	1000-2000	---	---	---	60-100	---
Nb (ppm)	5-300	10-65	10-400	10-400	49,600	51,000	9,500	100-150	<0.0002
Mo (ppm)	80-5500	20,000-30,000	2000-3000	30,000	27,000	30,000	---	<200-800	0.0002-0.002
Sn (ppm)	<200	---	---	---	---	---	3000	12,000-30,000	0.0016-0.0020
Ag (%)	<0.0002	<0.0005	---	---	---	---	---	---	80
In (%)	---	---	---	---	---	---	---	---	15
Cd (%)	---	---	---	---	---	---	---	---	5
Cl (ppm)	<50-130	---	---	---	---	---	---	---	---

Note: Adapted from Bedore, Levin and Tuite 1987; Roberts 1981; Evans, et al. 1984; Lepel, et al. 1995; Robertson, et al. 1991)

systems. The long-lived isotope ^{36}Cl (3.01E5 year) can be produced in neutron-irradiated metals in small, but perhaps significant amounts.

The boron carbide used in BWR control rod blade assemblies and the borosilicate glass used in PWR Burnable Poison Rod Assemblies (BPRA) are used for neutron absorption for reactor control. The ^{10}B isotope in these materials is the source of long-lived ^{10}Be (1.6E6 year half-life) in the neutron poison materials, being produced by the reaction ^{10}B (n,p) ^{10}Be.

2.1.2 Long-Lived Neutron Activation Products

The long-lived neutron activation products produced in irradiated structural materials in nuclear power systems, together with their half-lives, primary production modes, and principal radiations are listed in Table 2.4. Included in the table are the radionuclides specifically listed in 10 CFR Part 61 (except the TRU isotopes), plus a number of additional long-lived neutron activation products which are generated in a variety of reactor construction materials. Some of these additional radionuclides may be produced in activated metal and primary cleanup resin LLW in quantities that could require further environmental and dosimetric assessment with respect to their disposal in shallow-land burial facilities. For this reason it was deemed prudent to conduct empirical measurements of these radionuclides in a number of activated metal and primary cleanup resin LLW materials to provide a more reliable data base. These radionuclides are discussed individually in more detail in Section 3 of this report.

2.2 Neutron Activation of Corrosion Products Released to Reactor Coolant

The reactor construction materials discussed in Section 2.1.1 represent the source-term for the long-lived radionuclides that are present in reactor coolant water. These radionuclides enter the primary coolant

via two main mechanisms: 1) corrosion reactions between neutron-activated metal components within the reactor pressure vessel and the coolant water release soluble or particulate neutron activation products to the coolant, and 2) trace metals released from reactor construction materials outside of the neutron flux region of the reactor are carried to the reactor core in the cooling water where the metals are neutron-activated.

The soluble radionuclide species and a fraction of the particulate radionuclides are removed from the primary coolant by two main mechanisms: 1) plate-out on the inner surfaces of the primary loop piping and other components, and 2) removal from the primary coolant by adsorption onto primary demineralization resins and by filtration onto primary filters used for cleanup of the primary coolant. These ion exchange resins and primary filters represent some of the most radioactive low-level waste types generated at nuclear power stations, and are the major contributors, along with neutron-activated metal waste, to the radionuclide inventory at low-level waste disposal facilities. Essentially the same radionuclides that are produced in the neutron-activated metal components are present in the spent primary resins and filters (see Table 2.4). Fission products are also released to the reactor coolant via recoil from the trace uranium contamination on fuel assemblies or escape of fission products through fuel cladding defects or failures. All of these radionuclides also enter a wide variety of other types of low-level waste, including sludges, dry active waste, secondary resins, and evaporator concentrates. The volumes, activities, and sources of these low-level waste types that are generated at commercial nuclear power stations have been reported in detail (Daloisio and Deltete 1988).

Table 2.4 Long-Lived Neutron Activation Products in Structural Materials in Nuclear Power Systems

Radionuclides Specified in 10CFR61

Radionuclide	Half-life (yr)	Primary Production Mode(s)	Principal Radiations
^{3}H	12.3	^{6}Li(n,α)^{3}H	18.6 keV β^-
^{14}C	5730	^{14}N (n,p) ^{14}C ^{13}C(n,γ)^{14}C	157 keV β^-
^{59}Ni	7.6E4	^{58}Ni(n,γ)^{59}Ni	6.93 keV x-ray
^{63}Ni	100	^{62}Ni (n,γ)^{63}Ni	66.9 keV β^-
^{60}Co	5.27	^{59}Co (n,γ)^{60}Co	318 keV β^-; 1173 keV and 1333 keV γ's
^{90}Sr-^{90}Y	29.1	^{235}U fission	546 keV and 2281 keV β^-s
^{94}Nb	2.0E4	^{93}Nb (n,γ)^{94}Nb	473 keV β^-; 703 keV and 871 keV γ's
^{99}Tc	2.13E5	^{98}Mo (n,γ) ^{99}Mo$\rightarrow^{99}$Tc ^{235}U fission	292 keV β^-
^{129}I	1.57E7	^{235}U fission	150 keV β^-; 29.8 keV x-ray
^{137}Cs-^{137}Ba	30.17	^{235}U fission	514 keV β^-; 662 keV γ

Table 2.4 (Continued)

Additional Long-Lived Radionuclides Not Specified in 10CFR61

Radionuclide	Half-life (yr)	Primary Production Mode(s)	Principal Radiations
^{10}Be	1.6E6	^{10}B (n,p)^{10}Be	556 keV β^-
^{36}Cl	3.01E5	^{35}Cl (n,γ) ^{36}Cl	709 keV β^-
^{93m}Nb	16.1	^{93}Nb (n,n') ^{93m}Nb	16.5 kev x-ray; 30 kev γ
^{93}Mo	3500	^{92}Mo (n,γ) ^{93}Mo	16.5 keV x-ray; 30kev γ
^{108m}Ag	130	^{107}Ag (n,γ) ^{108m}Ag	434 keV, 614 keV, and 723 keV γ;s
^{113m}Cd	14.1	^{112}Cd (n,γ) ^{113m}Cd	590 keV β^-
^{121m}Sn	55	^{120}Sn (n,γ) ^{121m}Sn	354 keV β^-; 26.3 keV x-ray

3 Long-Lived Radionuclides Not Considered in 10 CFR Part 61 in Low-Level Waste

A number of long-lived radionuclides, not specifically addressed in 10 CFR Part 61, are produced in neutron-activated metal components in significant concentrations. These radionuclides are generally beta emitters or low-energy photon emitters and are normally present in trace amounts in the usual types of low-level waste. However, in specific types of low-level waste which are infrequently encountered in commercial nuclear power stations waste streams, these radionuclides can take on major proportions. Seven of these radionuclides are discussed below.

3.1 Beryllium-10

Beryllium-10 is a very long-lived (1.6E6 year half-life) radionuclide which is a pure beta emitter (556 keV max. ß⁻). To the best of our knowledge, this radionuclide has never been measured in LLW from nuclear power stations prior to this study. Because of its very long half-life, it will, for all practical purposes, always remain with certain types of LLW. Therefore, it is important to empirically determine the concentrations of this radionuclide in the special types of waste in which it is generated.

Beryllium-10 can be produced by several nuclear reactions, including the following:
^{9}Be (n, gamma) ^{10}Be, ^{9}Be (d, p) ^{10}Be, ^{10}B (n, p) ^{10}Be, ^{11}B (n, d) ^{10}Be, ^{11}B (n, np) ^{10}Be, and ^{13}C (n, alpha) ^{10}Be. The ^{9}Be (n, gamma) ^{10}Be reaction is probably of minimal importance because there are no significant sources of beryllium parent material present in components of nuclear power stations. The (n, d), the (n, np), and the (n, alpha) reactions have very high energy thresholds for these reactions and therefore will also be minimally important.

For nuclear power station LLW, the ^{10}B (n, p) ^{10}Be reaction is probably the most important for producing ^{10}Be because of its lack of an energy threshold for this reaction. The (n, p) cross section for this reaction is given in Figure 3.1. The figure shows this cross section to be several tens of millibarns at thermal neutron energies and at neutron energies above about 1 meV. Therefore, this reaction does have high enough cross section values at appropriate

neutron energies for a fission neutron spectrum to produce significant amounts of ^{10}Be. Also, the parent isotope, ^{10}B, is present in spent BWR control rod blades as boron carbide (B_4C), in spent PWR Burnable Poison Rod Assemblies as borosilicate glass, and is used as a chemical reactivity shim in PWR primary coolant as a soluble borate at concentrations of up to several thousand parts-per-million of boron. Therefore, ^{10}Be can be produced from the ^{10}B in spent control rod assemblies and in PWR primary coolant. Once the ^{10}Be is produced in the primary coolant, it is capable of then entering into most of the LLW streams generated at nuclear power stations, e.g., primary demineralization resins, filters, sludges, evaporator bottoms, etc.

3.2 Chlorine-36

Chlorine-36 is a very long-lived (3.01E5-year half-life) neutron activation product which primarily decays by emission of a 709 keV beta particle with no gamma radiations. Chlorine-36 is produced primarily by thermal neutron capture (43.6 barn cross section) by trace amounts of chloride impurities present in reactor construction materials and in reactor primary coolant via the reaction ^{35}Cl (n, gamma) ^{36}Cl. The concentrations of Cl in these materials are kept as low as possible because of the deleterious corrosion effects on metals due to Cl ion. Stainless steel Type 304 has Cl concentrations ranging from less-than 50 to 130 ppm (see Table 2.3), and reactor coolant Cl concentrations range from about 0.6 to 7 ppb (Cline 1996). Because of these low Cl concentrations, the quantities of ^{36}Cl produced in reactor materials and primary coolant are very low. Consequently, low-level wastes from nuclear power stations contain very low concentrations of ^{36}Cl, and it is not reported in waste classification manifests.

A few measurements of ^{36}Cl have been previously made in reactor coolant and primary demineralization resins at several Swiss BWR and PWR reactors (Liu, et al. 1991). This study reported ^{36}Cl/^{137}Cs activity scaling factors ranging from 1.4E-6 to 17.0E-6 for the coolant and resin samples

B-10 (n,p) Cross Section
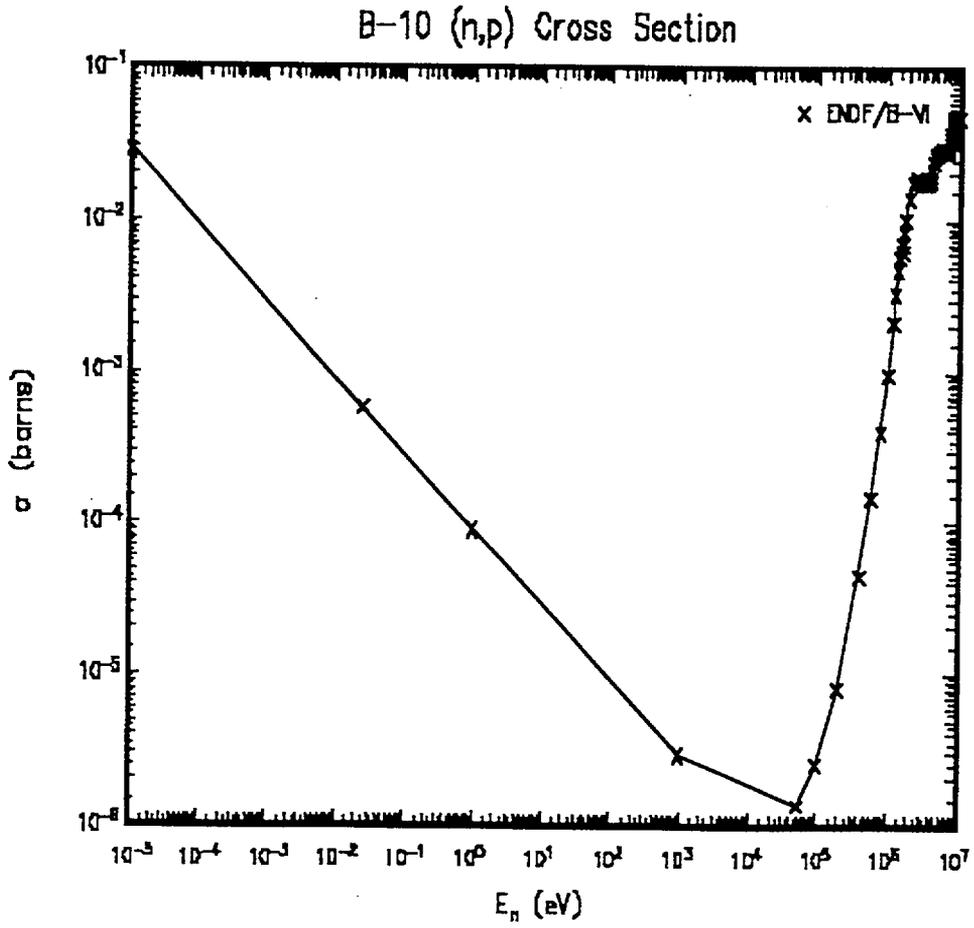
Figure 3.1 ^{10}B (n,p) Cross Section as a Function of Neutron Energy

However, because of its very long half-life, its high degree of environmental mobility, and its relatively energetic beta particle emissions, ^{36}Cl is of concern since it will eventually migrate from a low-level waste disposal facility. Site performance assessment modeling has shown that less than Curie amounts of ^{36}Cl disposed at a LLW disposal facility are enough for ^{36}Cl to become the most significant radiation dose contributor to the general public for the groundwater/domestic well transport-exposure scenario (Campbell 1995).

3.3 Molybdenum-93

Molybdenum-93 is a very long-lived (3500 year half-life) neutron activation product which is produced by thermal neutron capture by ^{92}Mo. Molybdenum is found in stainless steel at concentrations of about 2600 ± 1500 ppm, and Inconel contains about 30,000 ppm of Mo. The ^{93}Mo decays through an 80% transition by electron capture to 13.6 year ^{93m}Nb. The ^{93m}Nb decays with the emission of 16.5 keV Nb x-rays. Data from recent reactor hardware analyses gave ^{93}Mo/^{60}Co activity scaling factors for stainless steel of about 2E-5 and for Inconel of about 2E-4 (Robertson, Thomas, Wynhoff, and Haggard 1993; Lepel, Robertson, Thomas, Pratt, and Haggard 1995). After several thousand years, ^{93}Mo will be a significant radionuclide in activated metal wastes after the ^{60}Co (5.27 year half-life) and ^{63}Ni (100 year half-life) have decayed.

3.4 Niobium-93m

Niobium-93m is produced by the reaction ^{93}Nb (n, n') ^{93m}Nb, by beta decay of ^{93}Zr, and by the electron capture decay of ^{93}Mo. It is, therefore, produced by neutron activation of Nb, Zr, and Mo. Niobium is present as an impurity in stainless steel and some Inconel types at concentrations of 5 to 400 ppm, and is present as an additive in some types of Inconel at 10,000 to 50,000 ppm (see Table 2.3). Niobium-93m has a half-life of 16.1 years, and decays with the emission of 16.5 keV Nb x-rays and a 30 keV gamma-ray. Because two of the ^{93m}Nb parents, ^{93}Mo and ^{93}Zr, have extremely long half-lives, the ^{93m}Nb will remain in some types of neutron-activated metal wastes for thousands of years. Analyses of neutron-irradiated stainless steel reactor hardware have

reported ^{93m}Nb/^{60}Co activity scaling factors of about 3E-3, while Zircaloy and some Inconel alloys have ratios of about 1.0 (Robertson, Thomas, Wynhoff, and Haggard 1993; Lepel, Robertson, Thomas, Pratt, and Haggard 1995).

3.5 Silver-108m

Silver-108m is a 130-year half-life radionuclide produced by the thermal neutron activation reaction ^{107}Ag (n, gamma) ^{108m}Ag. Silver is present at a concentration of 80% in the Ag-Cd-In alloy used in PWR control rod assemblies. Therefore, ^{108m}Ag is a major constituent of these types of spent control rod assemblies being replaced at PWR stations. The ^{108m}Ag decays with the emission of several high-energy gamma rays (434, 614, and 723 keV) and therefore has a relatively high Curie-to-dose rate conversion factor. Silver-108m is generally not a major constituent of other types of low-level waste, e.g., DAW, spent ion exchange resins, and sludges.

3.6 Cadmium-113m

Cadmium-113m is a 14.1-year half-life radionuclide produced by thermal neutron capture by the following reaction, ^{112}Cd (n, gamma) ^{113m}Cd. Cadmium is present at a concentration of 5% in Ag-Cd-In alloy used in PWR RCCA control rod assemblies. Therefore, ^{113m}Cd is a major constituent of spent control rod assemblies of this type, but is not generally a major constituent of other types of low-level waste. Cadmium-113m decays with the emission of a 590 keV beta particle with no accompanying gamma-ray emissions.

3.7 Tin-121m

Tin-121m is a 55-year half-life radionuclide produced by thermal neutron activation of tin, according to the reaction, ^{120}Sn (n, gamma) ^{121m}Sn. Tin is added to Zircaloy metal components at concentrations ranging from 1 to 3%, and is, therefore, a major constituent of neutron irradiated Zircaloy, but is not a major constituent of other types of LLW. Tin-121m decays with the emission of a 353 keV beta particle and an accompanying 26.3 keV x-ray.

4 Sampling and Analyses of Neutron-Activated Metal and Primary Resin Low-Level Wastes

During this study, five types of neutron-activated metal wastes and two types of spent ion exchange resin wastes were collected from nuclear power stations and analyzed for 10 CFR Part 61 radionuclides and other long-lived radionuclides not specifically mentioned in 10 CFR Part 61. This section describes the sampling and analyses of these highly radioactive specimens.

4.1 Sampling

This section describes the sampling of the activated metal wastes and the primary demineralization resins collected for the radiochemical analyses of the 10 CFR Part 61 radionuclides and the additional long-lived radionuclides of interest.

4.1.1 Neutron-Activated Metal Wastes

Neutron-activated metal waste samples from nuclear power stations were difficult to obtain within the scope and budget of this project. Because of the very high gamma dose rates associated with these types of waste samples, it was difficult to obtain specimens that could be packaged, shipped, and handled without resorting to the use of very expensive handling procedures and highly-shielded shipping casks. Nevertheless, five specimens of neutron-activated metal waste materials were obtained for this study. These samples are listed in Table 4.1, and consist of three stainless steel (Type 304) specimens cut from two different BWR control rod blades and a cladding sample from a Low Power Range Monitor (LPRM); an Inconel-600 spring specimen from a PWR Burnable Poison Rod Assembly (BPRA); and a small piece of the Ag-In-Cd alloy used in a PWR Rod Control Cluster Assembly (RCCA). As evidenced by the discharge date of these samples from the reactors, they had been stored in the reactor's spent fuel pool for a number of years prior to disposal to allow shorter-lived radionuclides to decay and thus provide samples with manageable gamma dose rates.

The specimens of the LPRM and the control rod blade from Peach Bottom Station were cut from the whole components stored in the spent fuel pool at the reactor station and then shipped in shielded 55-gallon steel shipping drums to PNNL. The control rod blade from Duane Arnold Station and the BPRA and RCCA assemblies from Point Beach Station were shipped as whole components from the reactor stations to PNNL in special shipping casks as part of another program at PNNL sponsored by the DOE Office of Civilian Radioactive Waste Management. At PNNL all samples were unloaded into heavily shielded hot-cell facilities for further sub-sampling and preliminary cleaning of the small specimens. Following radiological analyses, all samples were disposed of as LLW at the Hanford DOE LLW disposal facility.

Metal sub-samples were cut from the components, producing small pieces (several grams) which allowed for easier handling outside of the hot-cells and reduced the gamma dose rate from the sub-samples. The metal pieces were then very carefully cleaned in the hot-cell by repeatedly rinsing with a hot mixture of nitric/hydrochloric acid to decontaminate them from fission products and transuranic radionuclides that were present in the hot-cell in which the samples were prepared. The sub-samples were removed from the hot-cells and a second identical cleaning operation was conducted in an uncontaminated laboratory fume hood to insure complete decontamination from hot-cell radioactive material. Each metal sample was then either entirely dissolved or partially dissolved in appropriate acid mixtures and each stock solution was then brought to a total volume of 100 mL in volumetric flasks. The stock solutions were then used for radiochemical analyses of the radionuclides of interest listed in Table 4.2.

Table 4.1 Neutron-Activated Metal Waste Samples for Radiological Characterization

Sample No.	Metal Waste Type	Discharge Date	Reactor Station	Materials Sampled
#39	Stainless steel cladding from LPRM[1]	1976	Peach Bottom	Stainless steel Type 304
#40	Stainless steel cladding from control rod blade	3/89	Peach Bottom	Stainless steel Type 304
#43	Stainless steel cladding from control rod blade	10/88	Duane Arnold	Stainless steel Type 304
#41	Inconel spring from BPRA[2] component	11/75	Point Beach - 1	Inconel-600
#42	Ag-Cd-In alloy from RCCA[3] component	4/85	Point Beach - 1	Ag (80%) Cd (5%) In (15%) alloy

(1) LPRM = Low Power Range Monitor
(2) BPRA = Burnable Poison Rod Assembly
(3) RCCA = Rod Control Cluster Assembly

Table 4.2 Spent Ion Exchange Resin Samples for Radiological Characterization

Sample Number	Discharge Date	Reactor Station	Resin Type
Bead Resin #23	12/93	Crystal River - Unit 3	Reactor Water Cleanup (RWCU)
Powdered Resin #22	3/93	WNP-2	EDRFDR[1] Composite + RWCU[2] Composite
Bead Resin 2-2	4/96	Diablo Canyon	Mixed-Bed Demin Resin 2-2

(1) EDRFDR = Equipment Drain Radioactive - Floor Drain Radioactive
(2) RWCU = Reactor Water Clean Up

4.1.2 Primary Demineralization Resin Wastes

The ion exchange resin LLW samples used for this study are listed in Table 4.2.
The samples were packaged in shielded 5-gallon steel shipping cans at the nuclear power stations and shipped to PNNL. At PNNL the resin samples were transferred to clean laboratory fume hoods and prepared for radiochemical analyses.

The representative aliquoting of the solid ion exchange resins for radiochemical analyses was a difficult task that required great care in minimizing inhomogeneities in the radionuclide content of the sub-samples for analyses. Each resin sample was thoroughly mixed, coned, and divided into separate aliquots for the various radionuclide analyses. Each of the aliquots was then gamma counted to determine the concentrations of the gamma-emitting radionuclides and to ascertain the representativeness of each aliquot. It was assumed that since the gamma-emitters included both fission and activation products, that the homogeneity of the gamma-emitters would be analogous for the non-gamma-emitters.

This assessment showed that the aliquoting procedure provided separate aliquots that were very representative of one another. The major gamma-emitters in the powdered resin aliquots showed that the individual sub-samples varied from one another by only 1.2% to 11.5 % (percent standard deviation at the 95% confidence level), with the higher values due to relatively low counting statistics from some of the trace radionuclides . The bead resin sample provided a variance of only 3.3% to 5.0% (percent standard deviation at the 95% confidence level), indicating very representative sub-sampling of the resin. If the variance in the concentrations of the non-gamma-emitters is similar to that observed for the gamma-emitters, then it would be expected that the real variance in all radionuclides in the aliquoted sub-samples would not exceed the observed variance for the gamma-emitters, e.g., ranging from approximately 2% to 5% for most radionuclides. Thus, it appears that any slight inhomogeneities in radionuclide concentrations in the aliquots should not significantly bias the results of the radiochemical measurements.

The various resin aliquots were then used for radiochemical analyses of the radionuclides listed in Table 4.2.

4.2 Summary of Radioanalytical Procedure Development for Additional Radionuclides

This section provides a summary of the radioanalytical procedures that were developed for this project for the measurement of 10 CFR Part 61 and other long-lived radionuclides present in various types of low-level waste from nuclear power stations. More detailed step-by-step radioanalytical procedures for these radionuclides are given in Appendix A.

Beryllium-10

Beryllium-10 is removed from the acid leach of resins and dissolution of metals by precipitating with NH_4OH, dissolving the precipitate (ppt) in 6M HCl and passing the solution through an anion column which removes most of the transition metals. Beryllium-10 is reprecipitated with NH_4OH and the ppt dissolved in 0.1M HCl. Ultima Gold® scintillator is added and the ^{10}Be measured in a Quantulus® beta spectrometer. Yields are determined by ^7Be tracer.

Chlorine-36

Chlorine-36 is separated from HCl leach of the resin and the metal dissolution by adjusting the solution to 1M HCl and passing it through a cation resin column. Mercurous nitrate is added to the effluent of the column and Hg_2Cl_2 is precipitated. The ppt is washed, centrifuged, slurried with water, and transferred to a liquid scintillation vial. The slurry is suspended in Insta-Gel® scintillation cocktail and the ^{36}Cl beta measured in a Quantulus® liquid scintillation beta spectrometer. Yields are determined using ^{38}Cl tracer.

Iron-55

Iron-55 is removed from the acid leach of the resin or

the acid dissolution of the metal by successive precipitating with NH_4OH. The ppt is dissolved in 4M HCl and passed through an anion resin column where the iron is retained. Iron is then removed from the column by eluting with 0.01M HCl. The iron yield is determined gravimetrically and then the iron is transferred to a scintillation vial with Ultima Gold®, and the ^{55}Fe measured in a beta scintillation spectrometer.

Nickel-59 and Nickel-63

Nickel-59-63 is acid-leached from resin or metal samples are dissolved in appropriate acids. The acid solution is made basic after addition of iron carrier and nickel is scavenged by an iron hydroxide ppt with NH_4OH. The solution is evaporated to just dryness, made just basic with NH_4OH (pH 9), tartrate ion and NH_4Cl solutions are added. Saturated dimethyl glyoxime in alcohol is added to ppt the Ni dimethyl glyoxime. The ppt is dissolved in nitric acid and evaporated to near dryness. HCl is added with a drop of H_2SO_4 and evaporated to just dryness, pH 9 NH_4OH is added, ammonium tartrate added, and Ni dimethyl glyoxime is precipitated. Once again the Ni precipitate is dissolved in nitric acid and converted to the chloride. The residue is dissolved in water which is divided into two equal parts. One part is placed in a scintillation vial, Ultima Gold® scintillator added, and the sample beta counted for ^{63}Ni in a liquid scintillation spectrometer. The other portion is put in a beaker and sulfuric acid and thymol blue indicator added. The solution is adjusted with NH_4OH until a gold-green end-point and the nickel is electroplated on a tared disk. Yield is determined gravimetrically and the electroplated nickel is counted in a intrinsic germanium low energy gamma spectrometer for measurement of ^{59}Ni x-rays.

Niobium-93m

Niobium-95 tracer, Ni, Sr, Fe, Co, Sb, and Nb carriers are added to an aliquot of acid leachate or dissolution sample. The sample is then made basic with carbonate-free sodium hydroxide, and the resulting ppt is centrifuged. The precipitate is dissolved in hydrofluoric acid, and Co and Sb carriers are again added. The sample is transferred to a beaker containing concentrated nitric acid and

heated with stirring until the volume of acid is reduced to half. The sample is cooled and transferred to a centrifuge tube and the resulting ppt centrifuged. The precipitate is washed three times with water and then redissolved in HF. The sample is again transferred to a beaker containing concentrated nitric acid and heated with stirring until the volume is reduced to half. The precipitate is then washed twice with water and transferred to a 2-inch diameter planchet and dried. The planchets are covered with two layers of thin Mylar® plastic sheets and counted on the Low Energy Photon Spectrometer (LEPS) detector to determine the ^{93m}Nb. The samples are then counted on the gamma detector for 1000 minutes to determine the ^{94}NB, and the ^{95}Nb yield tracer.

Strontium-90

Cobalt and cesium carriers and ^{85}Sr tracer are added to an aliquot of each acid leachate or dissolution sample. The samples are brought to dryness, wet ashed, and dissolved in 8M nitric acid. Sr-Spec® columns are conditioned with 8M nitric acid and the samples loaded onto the columns. After the samples have passed through the columns, they are washed with 50 mL of 8M nitric acid. The columns are then heat-sealed in plastic and counted on an intrinsic germanium gamma detector to determine whether or not any ^{60}Co or ^{137}Cs remained in the sample. If no ^{60}Co or ^{139}Cs is detected, five more mL of acid is passed through the columns. The time of the last wash is recorded. The Sr is then eluted with 10 mL of water and collected in a liquid scintillation vial. The samples are counted on the gamma detector to determine the ^{85}Sr recovery. They were then evaporated to dryness under a heat lamp and 15 mL of Ultima Gold® liquid scintillation cocktail is added to each vial. The samples are counted in the Quantulus® liquid scintillation spectrometer to determine the ^{90}Sr content.

Technetium-99 and Molybdenum-93

The ^{99}Tc and ^{93}Mo are separated from an aliquot of the acid leach of the resin or the acid dissolution of the metal by adjusting to 1M HCl, and passing the solution through a cation resin column. The effluent is passed through a TEVA-Spec® column where both the Tc and Mo are removed. The TEVA-Spec®

column is washed and the resin extruded into a preweighed plastic cup, dried, weighed, and covered with Mylar® plastic film and counted Mylar®-side down on a LEPS detector for determining the yield of the [99]Mo tracer. After the 67-hour [99]Mo tracer has decayed away, the sampled is recounted on the LEPS for measuring [93]Mo x-rays. The sample is then transferred to a scintillation vial, slurried with water, suspended in Insta-Gel® scintillation cocktail, and counted in a Quantulus® beta scintillation spectrometer for [99]Tc.

Cadmium-109 and Cadmium-113m

The [109]Cd and [113m]Cd are purified by scavenging interfering radionuclides from aliquots of the acid leachate of the resin and the acid dissolution of the metal by precipitating AgCl. The ppt is filtered and the supernate containing the Cd is then carried with $Fe(OH)_3$ from a slightly basic NaOH solution. The precipitate is dissolved in 1M HCl and passed through an anion resin column where the Cd is retained. After washing the column, the Cd is eluted with NH_4OH. The ammonium salts are destroyed and the residue is dissolved in 0.1M HCl, made pH 8 with NaOH, and thioacetamide is added to precipitate CDs. The CDs is counted in a gamma spectrometer to measure the [109]Cd and the [115]Cd tracer. The CDs is then evaporated to dryness with HNO_3 to destroy the sulfide, and the Cd converted to the chloride by evaporating to dryness with HCl. The residue is dissolved in 0.1M HCl and transferred to a scintillation vial where Ultima Gold® scintillator is added and the sample beta counted in a liquid scintillation spectrometer for [113m]Cd.

Plutonium-Americium-Curium-Uranium

Aliquots of the acid leach of the resin or acid dissolution of the metal are traced with [242]Pu, [243]Am, [232]U, and evaporated to dryness. The residue is dissolved in 3M HNO_3, made 0.1M with ferrous sulfamate and 0.1M with ascorbic acid, and passed through a TRU-Spec® column. The column is washed and the Am-Cm eluted with 4M HCl. The Pu is then eluted with 4M HCl which contains $TiCl_3$, and the U is eluted with 0.1M ammonium oxalate solution. Each fraction is evaporated to dryness, dissolved in 10 mL of 1M HCl, 100 ug Nd carrier added, and 1 mL HF added. Each fraction is filtered

through a polysulfone filter in which a solution containing 100 ug of NdF_3 has been passed through. The filters are mounted and counted in an alpha energy analyzer for the tracers and Pu, Am, Cm, and U isotopes.

Tin-121m

Am aliquot of each sample is placed in a beaker along with the following hold back carriers: Sn (II), Co, Ni, Nb and Cs. Then [117m]Sn tracer and 2-3 mL of conc. HCl are added and the samples are evaporated to dryness. Sulfuric acid and hydrogen peroxide are added and the samples taken to fumes. The samples are cooled, water is added, and the samples are chilled in an ice bath. Potassium iodide is then added to each sample and the tin is extracted twice into toluene. The tin is then back-extracted into a weak sulfuric acid solution, neutralized with sodium hydroxide, and precipitated as the sulfide using thioacetamide. The sulfide precipitate is destroyed with concentrated nitric acid, which results in tin oxide being formed. This oxide is washed with hot water, centrifuged, and slurried with a small amount of water. The samples are first counted on an intrinsic germanium gamma detector to determine the yield of the [117m]Sn, and then a liquid scintillation cocktail is added and the samples are counted in the Quantulus® liquid scintillation counter to determine the [121m]Sn content.

5 Concentrations of Additional Long-Lived Radionuclides in Low-Level Wastes

This section provides the radioanalytical results of the analyses of the five neutron-activated metal and three spent ion exchange resin samples. These analyses include the 10 CFR Part 61 radionuclides, plus the additional long-lived radionuclides discussed in Section 3. These long-lived radionuclides are of interest because new LLW disposal facilities will be designed to contain the wastes for hundreds of years before the facilities are breeched and infiltrated with groundwater. Therefore, those radionuclides having half-lives long enough to remain for hundreds of years will be those of greatest radiological concern to the surrounding public.

5.1   Neutron-Activated Metal Wastes

The radionuclide measurements of the five neutron-activated metal samples are given in Tables 5.1 and 5.2. Table 5.1 gives the neutron activation products measured in three samples of Type-304 stainless steel from two spent control rod blades and a spent Low Power Range Monitor (LPRM). These data provide not only 10 CFR Part 61 radionuclide analyses, but also measurements of a number of other long-lived radionuclides that are present in some types of activated metal components from nuclear power stations. For the stainless steel specimens, the concentrations of most of the additional long-lived radionuclides were very low or non-detectable.

The radionuclide concentrations for sample #43, the Duane Arnold Control Rod Blade (CRB) at the time of discharge from the reactor and their change in relative abundance with time are shown in Figure 5.1. As shown in the figure, ^{60}Co is initially the most abundant radionuclide but decays relatively rapidly. The ^{63}Ni becomes the most abundant radionuclide after 5 to 10 years and remains the most abundant for many hundreds of years. At about 700 years after discharge from the reactor, the concentrations of ^{63}Ni and ^{59}Ni become about equal and about two orders of magnitude greater than the next most abundant radionuclide, ^{10}Be.

These measurements of ^{10}Be are believed to be the first ever made for LLW materials. The ^{10}Be is produced by neutron activation of the boron in the boron carbide and borosilicate glass neutron-absorber materials in the Duane Arnold CRB and the Point Beach Burnable Poison Rod Assembly (BPRA), respectively, by the reaction, ^{10}B (n,p) ^{10}Be. Table 5.3 shows the ^{10}Be concentrations measured in these materials, together with the ^{60}Co concentrations for reference. For these types of boron-containing control rod assemblies, ^{10}Be will be the second most abundant activation product (next to ^{59}Ni) after about 1400 years of decay, and because of it's relatively energetic beta emissions (556 keV) it will be a major contributor to the radiation dose from these control rod components.

Of the additional long-lived radionuclides measured in the stainless steel specimens, only the ^{93m}Nb was detectable in all samples. As shown in Table 2.4, the ^{93m}Nb is produced by the reaction, ^{93}Nb (n, n') ^{93m}Nb on the stable niobium present in Type-304 stainless steel at concentrations ranging from 5 to 300 ppm. Although the concentrations of the ^{93m}Nb were initially about 70 times higher than the concentrations of the ^{94}Nb, after about 100 years the concentrations of the two radionuclides will be about equal, due to the much shorter half-life of ^{93m}Nb. After about 200 years, the ^{93m}Nb will become negligible in low-level waste.

The stainless steel from the Duane Arnold CRB contained a detectable amount of ^{113m}Cd. After about 175 years the ^{113m}Cd will be about the fifth most abundant activation product in this CRB. Although ^{109}Cd was also detected in this sample, it was much less abundant than the ^{113m}Cd and it's shorter half-life would not make it a significant contributor to the long-lived radionuclide inventory in CRBs.

A small amount of ^{93}Mo was detected in sample #43, but would never be a major radionuclide constituent or contributor to the radiation dose.

Concentrations

Table 5.1　　Long-Lived Neutron Activation Products in Irradiated Stainless Steel Low-Level Waste from Nuclear Power Stations

Radionuclide	Concentration (microcuries/gram of metal)*		
	#39 304 Stainless Steel LPRM[1] Peach Bottom	#43 304 Stainless Steel CRB[2] Duane Arnold	#40 304 Stainless Steel CRB[2] Peach Bottom
10CFR61 Radionuclides			
^{55}Fe	1.58±0.03E-2	6.83±0.21E2	2.10±0.06E0
^{59}Ni	1.00±0.17E-4	3.26±0.23E0	2.7±1.1E-3
^{63}Ni	1.07±0.08E-2	4.54±0.09E2	2.7±0.15E-1
^{60}Co	4.83±0.41E-2	1.49±0.043E3	3.61±0.04E-1
^{90}Sr	<2.0E-6	<2.9E-4	<2.1E-5
^{94}Nb	<1.3E-5	6.5±2.7E-3	<3.5E-4
^{99}Tc	<2.9E-6	4.08±0.33E-3	<1.8E-4
^{129}I	-	-	-
^{137}Cs	<2.0E-4	<9.2E-1	<6.3E-4
^{234}U	<1.6E-7	<1.1E-6	<1.7E-7
^{235}U	<8.1E-7	<1.9E-6	<8.8E-7
^{238}U	<1.7E-7	<1.8E-6	<2.2E-7
^{238}Pu	<3.5E-8	<1.2E-5	<2.3E-4
^{239,240}Pu	1.72±0.95E-7	2.9±1.1E-5	3.5±1.9E-5
^{241}Pu	<4.4E-5	<1.6E-3	<4.9E-5
^{241}Am	<2.6E-7	<1.8E-5	<6.7E-7
^{244}Cm	<3.8E-7	<2.7E-5	<1.0E-6
Additional Long-Lived Radionuclides			
^{10}Be	<5.3E-5	<2.2E-3	<8.2E-5
^{36}Cl	<3.7E-5	<1.8E-3	<7.2E-5
^{93}Mo	<2.5E-6	5.22±0.20E-4	<7.1E-6
^{93m}Nb	1.23±0.55E-4	4.48±0.32E-1	2.0±1.0E-3
^{108m}Ag	<2.4E-4	<1.4E0	<6.5E-4
^{109}Cd	<4.0E-5	6.4±2.2E-3	<1.2E-4
^{113m}Cd	<5.8E-5	9.3±1.8E-2	-
^{121m}Sn	-	-	<2.1E-4

(1)　LPRM = Low Power Range Monitor; 304 Stainless steel cladding; discharged 1976.
(2)　CRB = Control Rod Blade; 304 Stainless steel cladding; discharged 10/88.
*　Concentration on June, 1996

Table 5.2   Long-Lived Neutron Activiation Products in Irradiated Metal Low-Level Waste from Nuclear Power Stations

Radionuclide	Concentration (microcuries/gram of metal)*	
	#41 Inconel BPRA Spring[1] Point Beach	#42 Ag-Cd-In Alloy RCCA[2] Point Beach
10 CFR61 Radionuclides		
^{55}Fe	1.14±0.03E-1	6.76±0.20E-3
^{59}Ni	2.15±0.17E-1	1.39±0.62E-3
^{63}Ni	2.77±0.11E1	1.16±0.005E-1
^{60}Co	1.95±0.10E0	2.00±0.10E1
^{90}Sr	<3.2E-5	<2.3E-4
^{94}Nb	1.56±0.09E-3	<3.7E-4
^{99}Tc	<1.4E-5	2.92±0.37E-4
^{129}I	-	-
^{137}Cs	<4.6E-3	<2.0E-1
^{234}U	<4.1E-7	<1.2E-6
^{235}U	<5.9E-7	<7.1E-7
^{238}U	<1.4E-7	<4.6E-7
^{238}Pu	<9.3E-8	3.7±2.0E-7
^{239,240}Pu	1.6±0.5E-6	6.3±2.5E-7
^{241}Pu	<7.2E-5	<5.3E-4
^{241}Am	<5.4E-7	<3.3E-6
^{244}Cm	<8.1E-7	<4.5E-6
Additional Long-Lived Radionuclides		
^{10}Be	1.2±0.5E-4	<1.6E-4
^{36}Cl	3.95±0.95E-4	-
^{93}Mo	1.62±0.63E-4	<1.8E-5
^{93m}Nb	1.31±0.06E-1	3.5±1.6E-3
^{108m}Ag	<5.1E-3	6.37±0.19E2
^{109}Cd	1.4±0.3E-3	3.23±0.07E0
^{113m}Cd	1.28±0.03E-2	2.07±0.01E1
^{121m}Sn	<9.9E-5	<1.5E-3

(1)   BPRA = Burnable Poison Rod Assembly; discharged 11/75
(2)   RCCA = Rod Cluster Control Assembly; discharged 4/85
*   Concentration on June, 1996
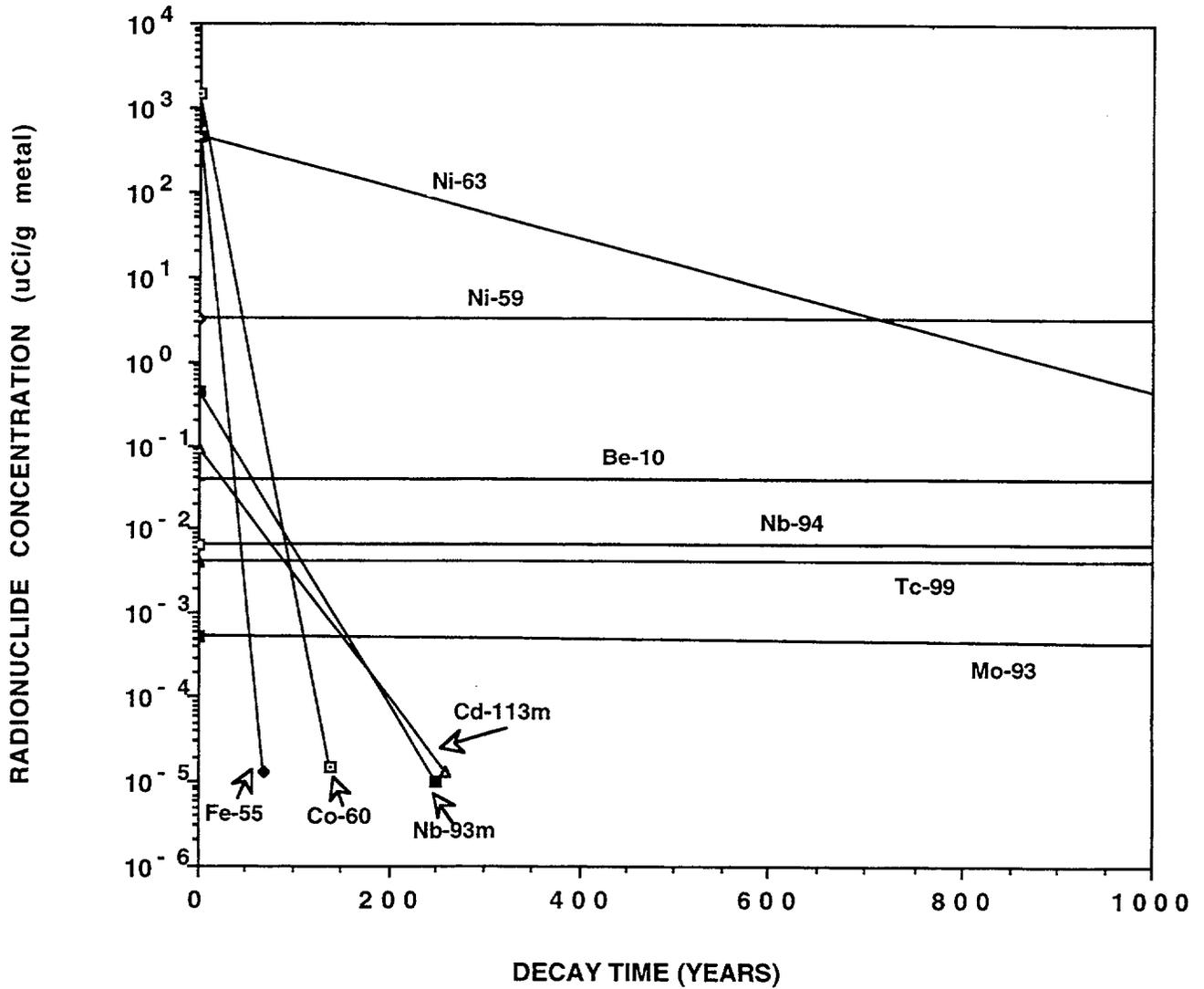
Figure 5.1   Change in Radionuclide Concentration with Time in 304 SS From Duane Arnold
Spent Control Rod Blade

Table 5.3 **Beryllium-10 and ^{60}Co Concentrations in Selected Boron-Containing LLW Samples**

| Sample | Material | Source | Concentration (μCi/g)* | | Activity Ratio |
			^{10}Be	^{60}Co	^{10}Be/^{60}Co
DER-1	boron carbide	Spent BWR Control Rod Blade Duane Arnold	3.68 ± 0.04E-2	10.2	3.61E-3
DER-2	boron carbide	Spent BWR Control Rod Blade Duane Arnold	3.91 ± 0.04E-2	5.47	7.15E-3
DER-4	borosilicate glass	Spent PWR BPRA Rod [a] Point Beach	2.72 ± 0.08E-3	5.12	5.31E-4
2-2	ion exchange resin	RWCU Resin[b] Diablo Canyon	8.22 ± 0.36E-3	8.70	9.45E-4

* Concentrations decay corrected to 5 years after discharge of components or materials from reactors

(a) BPRA = Burnable Poison Rod Assembly
(b) RWCU = Reactor Water Clean-Up

Concentrations

Tin-121m was not a significant constituent in spentCRB stainless steel, although it would be significant in neutron-irradiated Zircaloy materials used for fuel cladding and other reactor internal components.

Table 5.2 gives the radionuclide concentrations measured in two types of specialty alloys used in control rod assemblies. The Point Beach BPRA control rod uses springs made of an Inconel alloy. This specimen (sample #39) contains relatively high concentrations of ^{63}Ni and ^{59}Ni due to nickel being a major constituent (52 to 76%) in a variety of Inconel alloys. These two nickel radioisotopes will dominate the activation product abundances in Inconel alloys for many hundreds of years (see Figure 5.2). Niobium is also an added constituent (up to about 5%) in some Inconel alloys (see Table 2.3), and in sample #39, ^{93m}Nb and ^{94}Nb are major radionuclide constituents. After about 1500 years, the ^{94}Nb will be the second most abundant radionuclide in this Inconel, and because of it's relatively high-energy beta and gamma radiations, it will be a major contributor to the radiation dose from neutron-activated Inconel alloys containing niobium. Molybdenum-93 will also be a major long-lived radionuclide constituent, being produced by neutron activation of the percent levels of molybdenum present in Inconel alloys. Technetium-99 is also produced by neutron activation of molybdenum, and is present at about 10-fold lower concentration compared to the ^{93}Mo. Nevertheless, ^{99}Tc will be about the fifth most abundant radionuclide after about 300 years. The cadmium and tin radionuclides will never be major constituents of neutron-irradiated Inconel.

Another speciality metal associated with RCCA control rods is the silver (80%)-indium (15%)-cadmium (5%) alloy used as a neutron-absorber material. This material has a unique radionuclide composition following neutron irradiation. Silver-108m will be the dominant neutron activation product for many hundreds of years, and because of it's relatively high energy beta and gamma radiations, it will be the major dose contributor for this material (see Figure 5.3). Shortly after discharge, the cadmium radionuclides, ^{113m}Cd and

^{109}Cd, will be the next most abundant radionuclides, but the ^{109}Cd rapidly decays to insignificance. The ^{113m}Cd will be the second most abundant radionuclide up to about 150 years and then the ^{63}Ni becomes the second most abundant.

5.2 Primary Demineralization Resin Wastes

Next to neutron-activated metal wastes, primary coolant demineralization resin wastes from nuclear power stations contain the highest concentrations of radionuclides. These radionuclides are a mixture of neutron activation products and fission products. Table 5.4 provides the concentrations of 10 CFR Part 61 radionuclides, plus the additional long-lived radionuclides measured in this study in samples of PWR (sample #23) and BWR (sample #22) primary coolant demineralization resins.

The PWR resin (sample #23), a RWCU resin from Crystal River station contains predominantly ^{137}Cs, indicating minor release of fission products from the fuel. The change in radionuclide concentrations with time for this material is shown in Figure 5.4. After about 100 years, the ^{137}Cs and the ^{60}Co will have decayed below ^{63}Ni in concentration and the long-lived nickel radionuclides will be the most abundant for many hundreds of years. After about 1500 years, the ^{59}Ni will be the most abundant and ^{36}Cl will be the second most abundant radionuclide is this resin waste. The additional long-lived radionuclides measured in this study, except for the ^{36}Cl will never be major contributors to the radionuclide concentration or radiation dose from this material.

The BWR resin (sample #22), a mixture of RWCU and EDRFDR resins from WNP-2 nuclear power station is dominated by ^{60}Co for the first few decades. Nickel-63 and ^{137}Cs then become the most abundant radionuclides after about 30 to 150 years. Thereafter, the ^{63}Ni and ^{59}Ni will be predominant, followed by ^{94}Nb, ^{93}Mo, and ^{99}Tc which are all close in concentration. The additional long-lived radionuclides measured in this study will not be significant contributors to the concentration or radiation dose for this material.
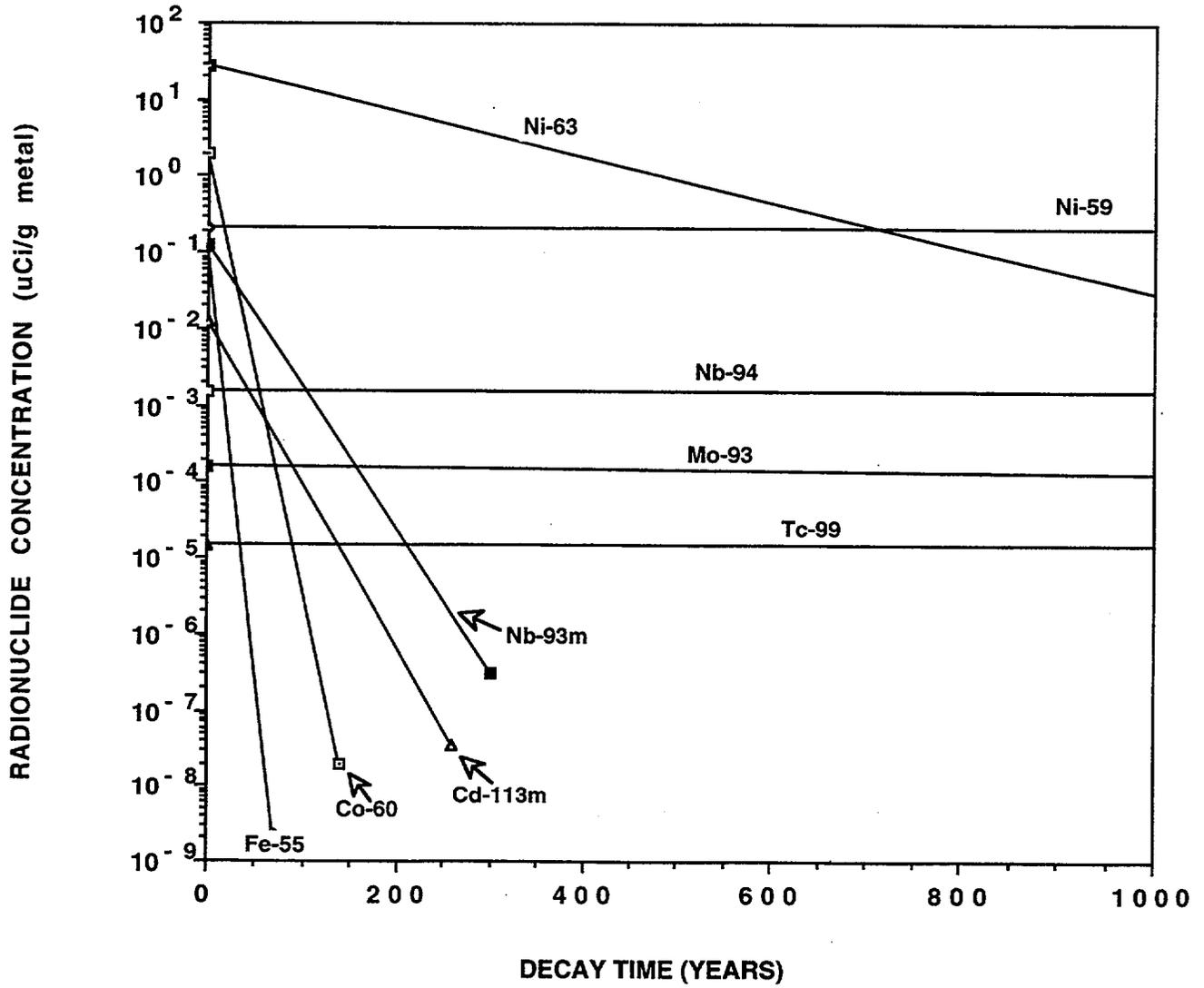
Figure 5.2   Change in Radionuclide Concentration with Time in Point Beach BPRA
Inconel Spring
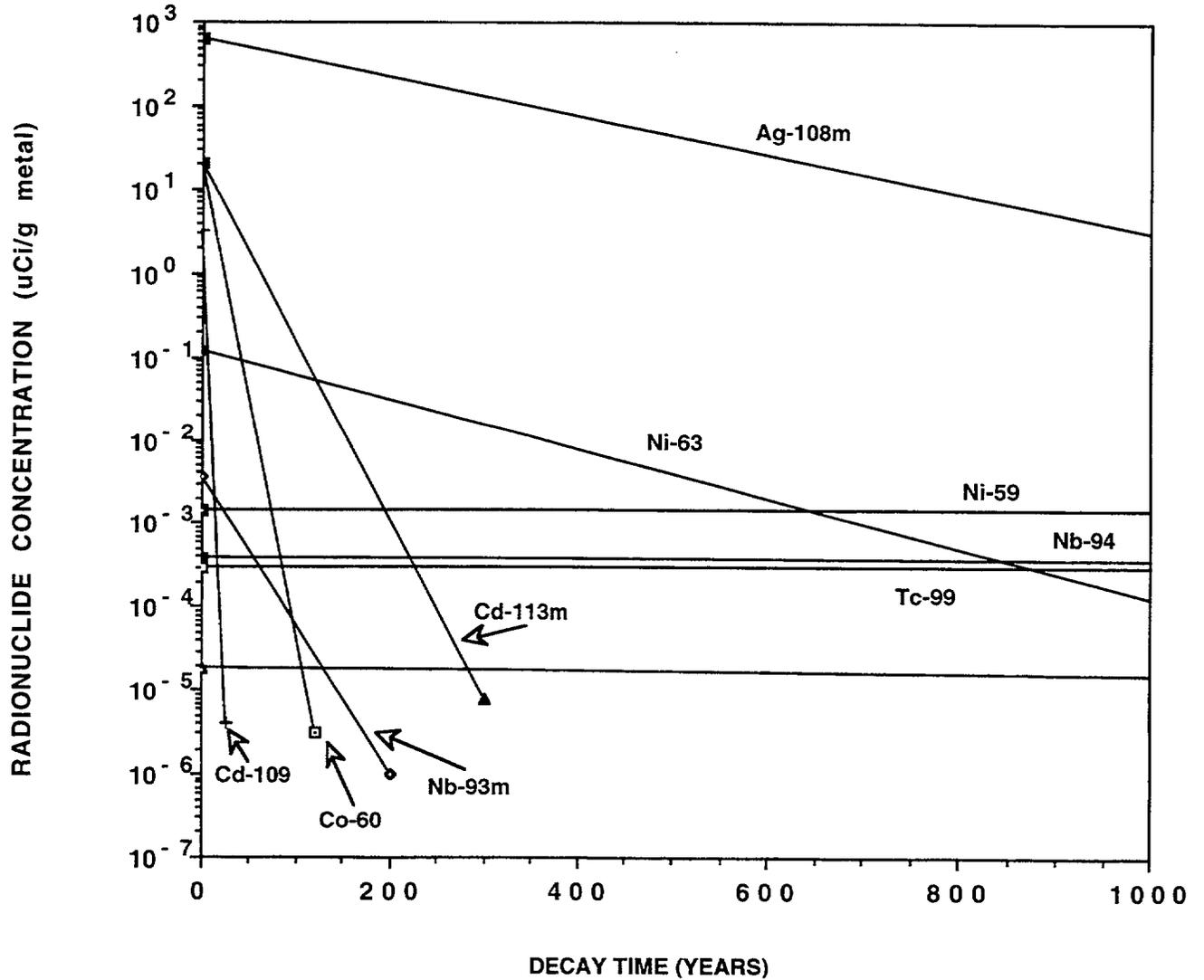
Figure 5.3   Change in Radionuclide Concentration with Time in Point Beach RCCA Ag-Cd-In Alloy
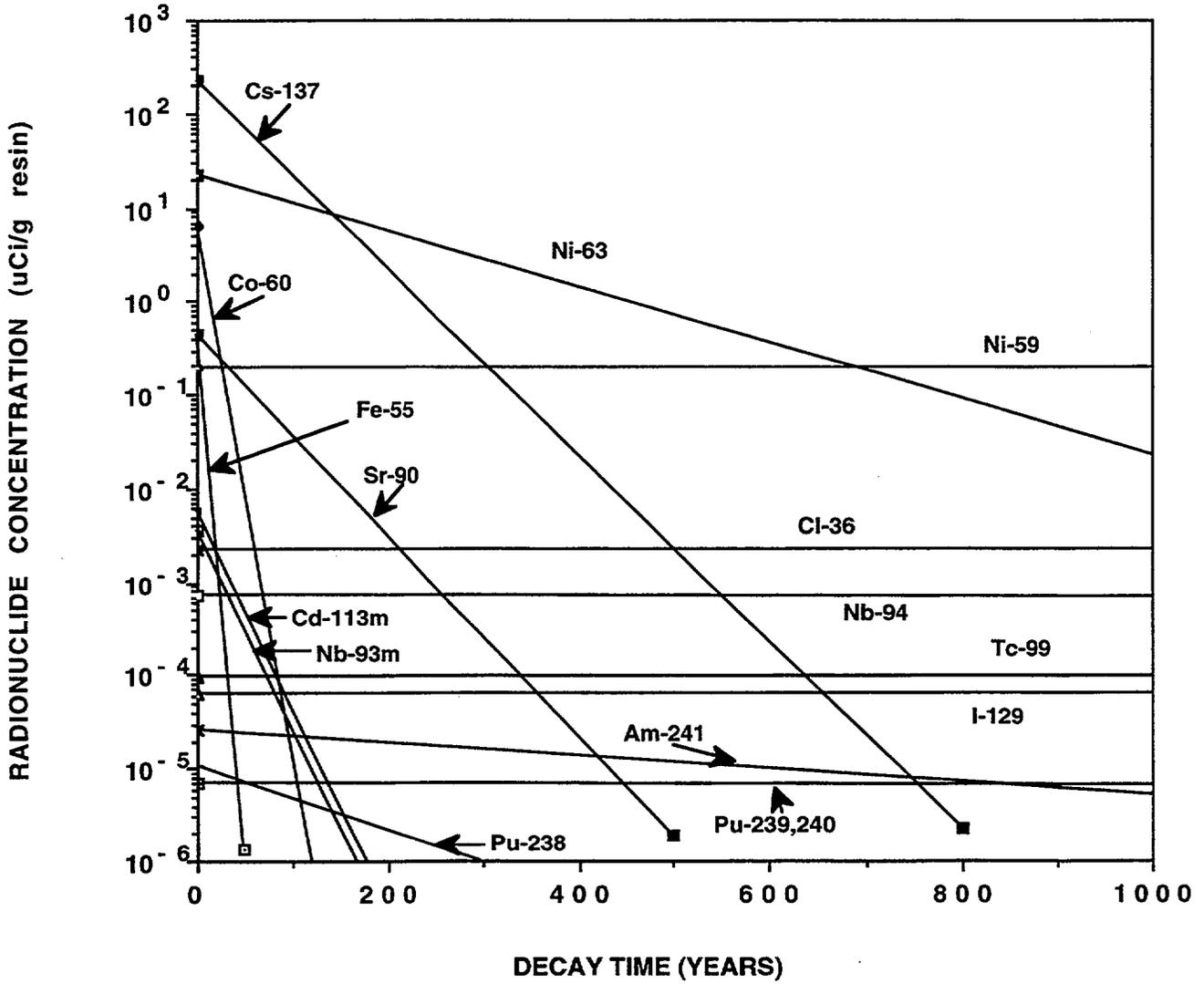
Figure 5.4   Change in Radionuclide Concentration with Time in Crystal River RWCU
Resin

Concentrations

Table 5.4   Long-Lived Neutron Activiation Products in Spent Ion Exchange Resins from Nuclear Power Stations

Radionuclide	Concentration (microcuries/gram of resin)*	
	#23 Bead Resin RWCU[1] Crystal River	#22 Powdered Resin EDRFDR[2]+RWCU Resins WNP-2
10 CFR61 Radionuclides		
^{55}Fe	4 48±0.04E-1	1.64±0.05E-1
^{59}Ni	1.91±0.09E-1	9.3±1.2E-3
^{63}Ni	2.25±0.07E1	8.90±0.23E-1
^{60}Co	6.40±0.14E0	2.77±0.08E1
^{90}Sr	4.48±0.39E-1	9.8±1.9E-3
^{94}Nb	<7.4E-4	<3.5E-4
^{99}Tc	9.7±3.3E-5	<2.2E-4
^{129}I**	6.51±0.07E-5	1.64±0.01E-7
^{137}Cs	2.23±0.09E2	6.17±0.19E-1
^{234}U	<2.4E-5	<2.1E-6
^{235}U	<9.9E-6	<1.1E-5
^{238}U	<3.3E-6	<6.4E-6
^{238}Pu	1.07±0.19E-5	<2.5E-6
^{239,240}Pu	7.0±1.4E-6	7.9±5.4E-6
^{241}Pu	<6.9E-4	-
^{241}Am	2.65±0.70E-5	<6.3E-6
^{244}Cm	9.3±4.1E-6	<9.9E-6
Additional Long-Lived Radionuclides		
^{10}Be	<1.08E-4	<7.9E-4
^{36}Cl	2.28±1.06E-3	<1.4E-2
^{93}Mo	<1.6E-5	2.6±1.0E-4
^{93m}Nb	3.7±1.6E-3	3.9±1.5E-3
^{108m}Ag	<5.0E-2	<1.3E-2
^{109}Cd	5.2±3.8E-4	<2.1E-2
^{113m}Cd	5.8±1.3E-3	1.71±0.58E-2
^{121m}Sn	<3.9E-4	<5.2E-3

*   Concentration on January, 1996
**   Measured by thermal emission mass spectrometry
(1)   RWCU = Reactor Water Clean Up; discharged 12/93
(2)   EDRFDR = Equipment Drain Radioactive-Floor Drain Radioactive; discharged 3/93

Another RWCU resin from Diablo Canyon nuclear power station that was prepared for disposal was also analyzed for several of the additional long-lived radionuclides, including ^{10}Be and ^{36}Cl (see Figure 5.6). The concentration units reported for this resin are in total mCi of each radionuclide in the entire resin shipment. Initially, ^{60}Co is the most abundant radionuclide, but after a few decades ^{14}C becomes, by far, the most abundant activation product, followed by ^{63}Ni, ^{59}Ni, ^{10}Be, and ^{94}Nb which will be the dominant radionuclides in this waste for thousands of years. The ^{36}Cl is a rather minor constituent of this resin, as are the fission product radionuclides, indicating very good fuel cladding integrity at Diablo Canyon station. This resin does illustrate that ^{10}Be will be one of the major long-lived radionuclides in spent RWCU resin wastes from reactor stations using high concentrations of boron in their primary coolant as a reactivity shim.
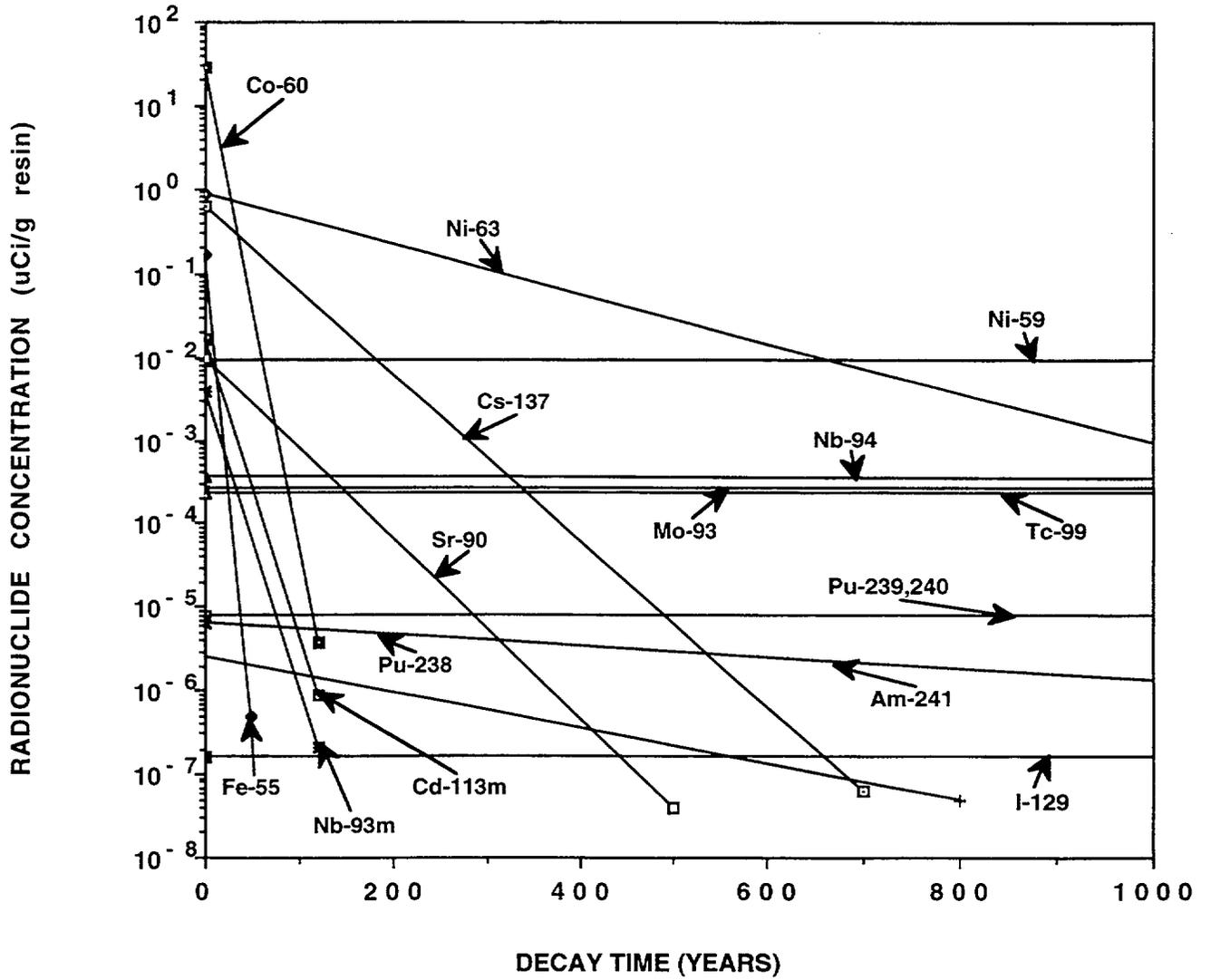
Figure 5.5   Change in Radionuclide Concentration with Time in WNP-2
EDRFDR+RWCU Resins
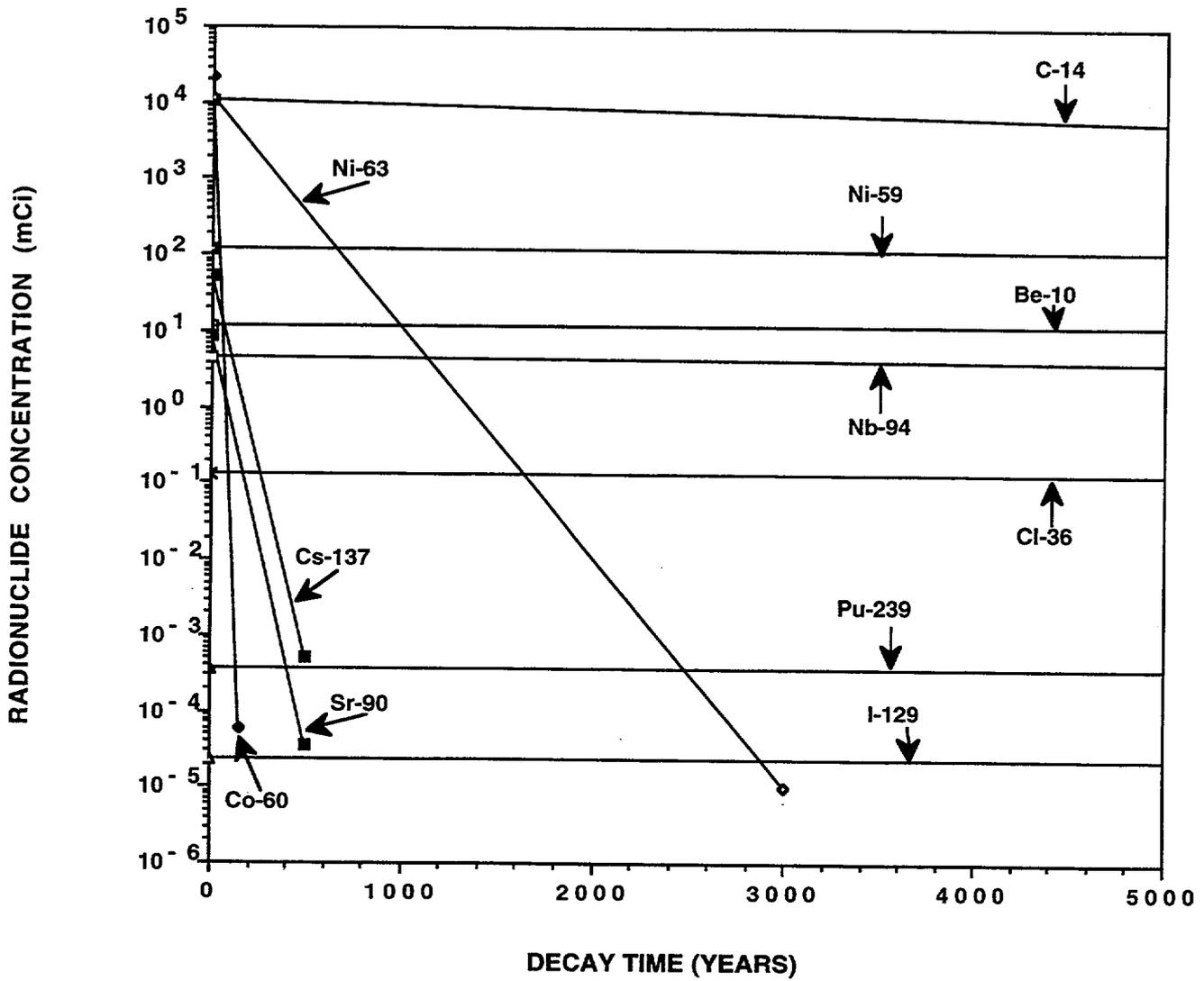
Figure 5.6   Decrease in Concentrations of Long-Lived Radionuclides in PWR Spent Ion Exchange Resin (RWCU)

6 Impact on Low-Level Waste Classification

The classification and disposal requirements of LLW are based, among other things, upon the concentrations of specified long-lived radionuclides in the waste. These radionuclides were selected because of their long half-lives, high environmental mobility, and potential to be present in wastes in significant concentrations. In addition to the specified radionuclides, a number of other long-lived radionuclides not included in 10 CFR Part 61 may be present in some types of wastes generated at commercial nuclear power stations. This study has identified a number of these additional radionuclides and this section provides an assessment of their impact upon 10 CFR Part 61 requirements.

The additional long-lived radionuclides identified in this examination of LLW materials, including neutron-activated metal wastes and primary resin wastes, appears to have minimal impact upon the requirements of 10 CFR Part 61. Of the additional radionuclides studied in this project, only ^{108m}Ag, ^{10}Be, and ^{36}Cl would appear to be of any significance from a low-level waste disposal and radiation dosimetric standpoint. The other long-lived radionuclides measured in this study (^{93}Mo, ^{93m}Nb, ^{113m}Cd, ^{121m}Sn) are present in sufficiently low concentrations and have relatively low dose conversion factors and environmental mobility, and thus do not appear to represent any significant potential hazard in the disposal of these LLW materials.

The relative concentrations of these radionuclides do not appear to be high enough to affect the waste classification criteria specified in 10 CFR Part 61. The potential radiation dose to the surrounding offsite general population is the primary concern of any additional radionuclides measured in LLW from nuclear power stations.

Table 6.1 lists the radiation dose conversion factors for the existing 10 CFR Part 61 radionuclides, plus the additional long-lived radionuclides measured in this study (Kennedy and Strenge, 1994). Of the group of additional radionuclides, ^{108m}Ag has the highest external dose conversion factor because of its three high energy, high abundance gamma-rays (see Table 2.4). Fortunately, the only major source of this radionuclide in LLW from nuclear power stations is

from spent Rod Cluster Control Assemblies (RCCA) from PWR stations. As discussed in Section 4, these control rod assemblies contain 80% silver, which is the parent material for the ^{108m}Ag. Thus, the potential LLW source term for this radionuclide will be somewhat limited. Nevertheless, it may be prudent to conduct a detailed assessment of ^{108m}Ag to determine if amendment into 10 CFR Part 61 would be warranted.

Beryllium-10 is produced from boron present in PWR primary coolant and in BWR and PWR control rods and will be continually present in LLW containing primary demineralization resins and spent control rods. Beryllium-10 has a relatively low external dose conversion factor because it is a pure beta emitter, but has moderately high inhalation and ingestion dose conversion factors. Because of its potential to be present in significant concentrations in LLW from nuclear power stations, ^{10}Be should be further evaluated to determine if it should be amended to the list of specified radionuclides in 10 CFR Part 61.

The external dose conversion factor for ^{36}Cl is also relatively low because it is a pure beta emitter, but the ingestion and inhalation dose conversion factors are moderately high. Because the main source of this radionuclide in LLW from nuclear power stations is the reactor primary coolant demineralizer resins, it will be ubiquitous in LLW in relatively small quantities. However, the high environmental mobility of this radionuclide will allow it to migrate from a LLW disposal site that has been infiltrated with groundwater. For this reason, it may be prudent to conduct a detailed assessment of ^{36}Cl to determine if it should be included in 10CFR61. An estimate of the yearly quantities of ^{36}Cl contained in spent primary resin LLW from all PWR stations in the U. S. can be estimated as follows. About 3.4E7 grams/year per PWR station of spent primary resins are generated for disposal. Using the range of ^{36}Cl concentrations measured in the two primary resins in this study (9.3E-5 to 3.4E-3 uCi/g), approximately 3200 to 78,000 uCi/year per PWR station are produced. Multiplying by the number of PWR stations in the U. S. (70) gives an estimated 0.2 to 5.5 Ci/year of ^{36}Cl contained in LLW from PWR stations. In a LLW site performance assessment modeling

Table 6.1   Dose Conversion Factors for 10CFR61 and Additional Long-Lived Radionuclides Measured
in Low-Level Waste (from Kennedy and Strenge, 1994)

Radionuclide	Ingestive (Sv/Bq)	Inhalation (Sv/Bq)	External (surface) $\frac{Sv/d}{Bq/m^2}$
10CFR61 Radionuclides			
^{14}C	5.64E-10	5.64E-10	1.39E-15
^{59}Ni	5.67E-11	7.31E-10	0
^{63}Ni	1.56E-10	1.70E-9	0
^{60}Co	7.28E-9	5.91E-8	2.03E-10
^{90}Sr	3.85E-8	3.51E-7	2.46E-14
^{90}Y	2.91E-9	2.28E-9	4.60E-13
^{94}Nb	1.93E-9	1.12E-7	1.32E-10
^{99}Tc	3.95E-10	2.25E-9	6.73E-15
^{129}I	7.46E-8	4.69E-8	2.23E-12
^{137}Cs	1.35E-8	8.63E-9	2.46E-14
^{238}Pu	8.65E-7	1.06E-4	7.23E-14
^{239}Pu	9.56E-7	1.16E-4	3.17E-14
^{240}Pu	9.56E-7	1.16E-4	6.93E-14
^{241}Am	9.84E-7	1.20E-4	2.37E-12
Additional Radionuclides			
^{10}Be	1.26E-9	9.58E-8	3.56E-14
^{36}Cl	8.18E-10	5.93E-9	5.81E-14
^{93}Mo	3.64E-10	7.68E-9	4.61E-13
^{93m}Nb	1.41E-10	7.90E-9	8.11E-14
^{108m}Ag	2.09E-9	4.18E-9	1.60E-10
^{113m}Cd	4.35E-8	4.13E-7	2.27E-14

To convert Sv/Bq to Rem/Ci or $\frac{Sv/d}{Bq/m^2}$ to $\frac{Rem/d}{Ci/m^2}$ multiply values in table by 3.70E12

exercise conducted by the NRC, modeling results, using a 0.1 Ci ^{36}Cl source term, indicated that this radionuclide would be the major contributor to the offsite ingestion radiation dose for the contaminated well/drinking water exposure scenario (Campbell, 1994). Thus, even though the relative quantities of ^{36}Cl in LLW are small compared to other radionuclides, it can be a major contributor to offsite radiation doses, and deserves further study to gain a better understanding of its radiological and environmental impacts from LLW disposal. Cadmium-113m has relatively high ingestion and inhalation dose conversion factors. However, because of its relatively short half-life (14.1 years) and the fact that it is present in LLW only in spent PWR Reactor Control Cluster Assemblies, further consideration for inclusion in 10 CFR Part 61 may not be warranted.

7 Determination and Review of Activity Scaling Factors

A common practice in the nuclear power industry is to use activity scaling factors for estimating the concentrations of difficult-to-measure radionuclides and determining their waste classification in LLW packages being prepared for disposal. Typically, a nuclear power station will periodically sample a variety of LLW types and submit them to service analytical laboratories for comprehensive 10 CFR Part 61 radionuclide analyses. Then the station will develop activity scaling factors for the difficult-to-measure radionuclides (pure beta emitters, low-energy photon emitters, and alpha emitters) relative to the most abundant long-lived gamma-emitting radionuclides present in the waste, usually ^{60}Co and ^{137}Cs, which are easily measured by gamma-ray spectrometry. A data base of scaling factors is then generated for the various sample types and used in conjunction with gamma-ray spectrometry to quantify the 10CFR61 radionuclides and determine their waste classification. Several data bases and assessments of activity scaling factors for the radionuclides specified in 10 CFR Part 61 in LLW from nuclear power stations have been published (Best and Miller, 1985, 1987; Cline, Noyce, Coe and Wright, 1985; Cline, Wright and Hollcroft, 1980; James and Vance, 1992; Robertson, et al., 1989; Vance, 1992; Vance, 1993; Vance, Helmholz and Sutherland, 1988; Vance, Holderness, James, and Lee, 1992).

A number of difficult-to-measure radionuclides lend themselves well to this activity scaling factor methodology, particularly neutron activation products (e.g., ^{55}Fe, ^{63}Ni, ^{59}Ni) which have similar production modes and similar physicochemical behavior in the reactor coolant and related waste streams compared to ^{60}Co. Other long-lived fission product radionuclides, such as ^{129}I, can be generically scaled to ^{137}Cs, whereas others are only marginally adapted to the use of scaling factors.

7.1 Determination of Activity Scaling Factors for Additional Radionuclides

There are a number of other long-lived difficult-to-measure radionuclides present in various types of LLW that are not specifically mentioned in 10CFR61. These radionuclides are usually (but not always) present as minor radionuclide constituents in LLW. For example, ^{108m}Ag and ^{113m}Cd are major radionuclide constituents in spent RCCA control rods composed of Ag-Cd-In neutron-absorbing alloy material, and ^{93m}Nb is a major constituent in neutron-irradiated high-niobium Inconel alloys. This section evaluates the potential use of activity scaling factors for additional long-lived radionuclides observed in various waste types.

7.1.1 Neutron-Activated Metal Radionuclides

7.1.1.1 Molybdenum-93

Molybdenum-93, which is produced by neutron activation of molybdenum present in stainless steel and some Inconel alloys, can generally be correlated rather well with ^{60}Co. However, the data base for this radionuclide in activated metals is quite limited, being confined to this study and to data published in NUREG/CR-6390 (Lepel, et al., 1995). Table 7.1 provides the measured concentrations of ^{93}Mo and ^{60}Co in the neutron-activated metal samples determined in this study, plus data taken from NUREG/CR-6390 (Lepel, et al., 1995). Although the absolute concentrations of these radionuclides vary by many orders of magnitude for the various activated-metal samples examined, the activity scaling factors for the ^{93}Mo/^{60}Co ratios were reasonably consistent, with a geometric mean of 1.62E-6. Figure 7.1 graphically shows the correlation of these two radionuclides for the samples listed in Table 7.1. This correlation is quite good, with only a few outlying data points, considering the wide range of sample types examined. Thus, the use of a generic activity scaling factor for nuclear power station LLW appears to be reasonable for this radionuclide pair.

Table 7.1 ^{93}Mo/^{60}Co Scaling Factors for Low-Level Waste

| ID No. | Sample | Material | Concentration (μCi/g)[a] | | Scaling Factor |
			^{93}Mo	^{60}Co	^{93}Mo/^{60}Co
DER-1	Duane Arnold CRB[b]	SS	1.49E-2	1.08E-4	1.38E-6
DER-1Z	"	SS	8.46E-3	8.37E-3	1.01E-6
DER-2	"	SS	7.82E-4	1.61E-3	4.86E-7
DER-2Z	"	SS	5.40E-3	4.79E-3	1.13E-6
DER-3	"	SS	<4.2E-4	2.03E-2	2.07E-6
DER-3Z	"	SS	<3.6E-4	1.14E-2	3.16E-6
DER-4(out)	Point Beach BPRA[c]	SS	5.17E-3	1.46E-4	3.54E-7
DER-4(in)	"	SS	1.92E-2	1.80E-3	1.07E-5
DER-5(out)	"	SS	7.42E-3	1.79E-4	4.15E-7
DER-5(in)	"	SS	1.22E-2	2.20E-3	5.55E-6
DER-6(out)	"	SS	2.53E-3	1.70E-4	1.49E-7
DER-6(in)	"	SS	9.89E-3	2.01E-3	4.92E-6
DER-10A	Point Beach RCCA[d]	SS	2.07E-2	4.54E-4	4.56E-7
DER-10B	"	SS	2.31E-2	5.69E-4	4.06E-7
DER-8	"	SS	1.44E-2	9.85E-3	1.46E-6
#39	Peach Bottom LPRM[e]	SS	<2.5E-6	3.71E-1	<6.90E-6
#43	Duane Arnold CRB	SS	5.22E-4	2.12E-3	2.46E-7
#40	Peach Bottom CRB	SS	<7.1E-6	4.84E-1	<1.48E-5
#41	Point Beach BPRA (Spring)	Inconel	1.62E-4	1.52E-1	1.07E-5

Table 7.1 (continued)

| ID No. | Sample | Material | Concentration (μCi/g)[a] | | Scaling Factor |
			[93]Mo	[60]Co	[93]Mo/[60]Co
#42	Point Beach RCCA	Ag-Cd-In	<1.81E-5	4.50E-1	<4.00E-7
#23	Cyrstal River RWCU Resin [f]	Resin	<1.6E-5	4.36E-0	<3.67E-6
#22	WNP-2 Resin	Resin	2.6E-4	2.08E-1	1.25E-5
				Mean *	3.76E-6
				Standard Deviation	4.52E-6
				Geometric Mean **	1.62E-6

(a) Concentrations decay-corrected to 5 years after discharge of components or materials from the reactor. It was necessary to sandardize the decay time after discharge from the reactors because some of the materials were quite old and the ^{60}Co had undergone substantial radioactive decay.
(b) CRB = Control Rod Blade
(c) BPRA = Burnable Poison Rod Assembly
(d) RCCA = Rod Cluster Control Assembly
(e) LPRM = Low Power Range Monitor
(f) RWCU = Reactor Water Clean-Up

Note: All DER sample data from NUREG/CR-6390 (Lepel, et al., 1995)

* Arithmetic mean of all 22 values

** Geometric mean of all 22 values
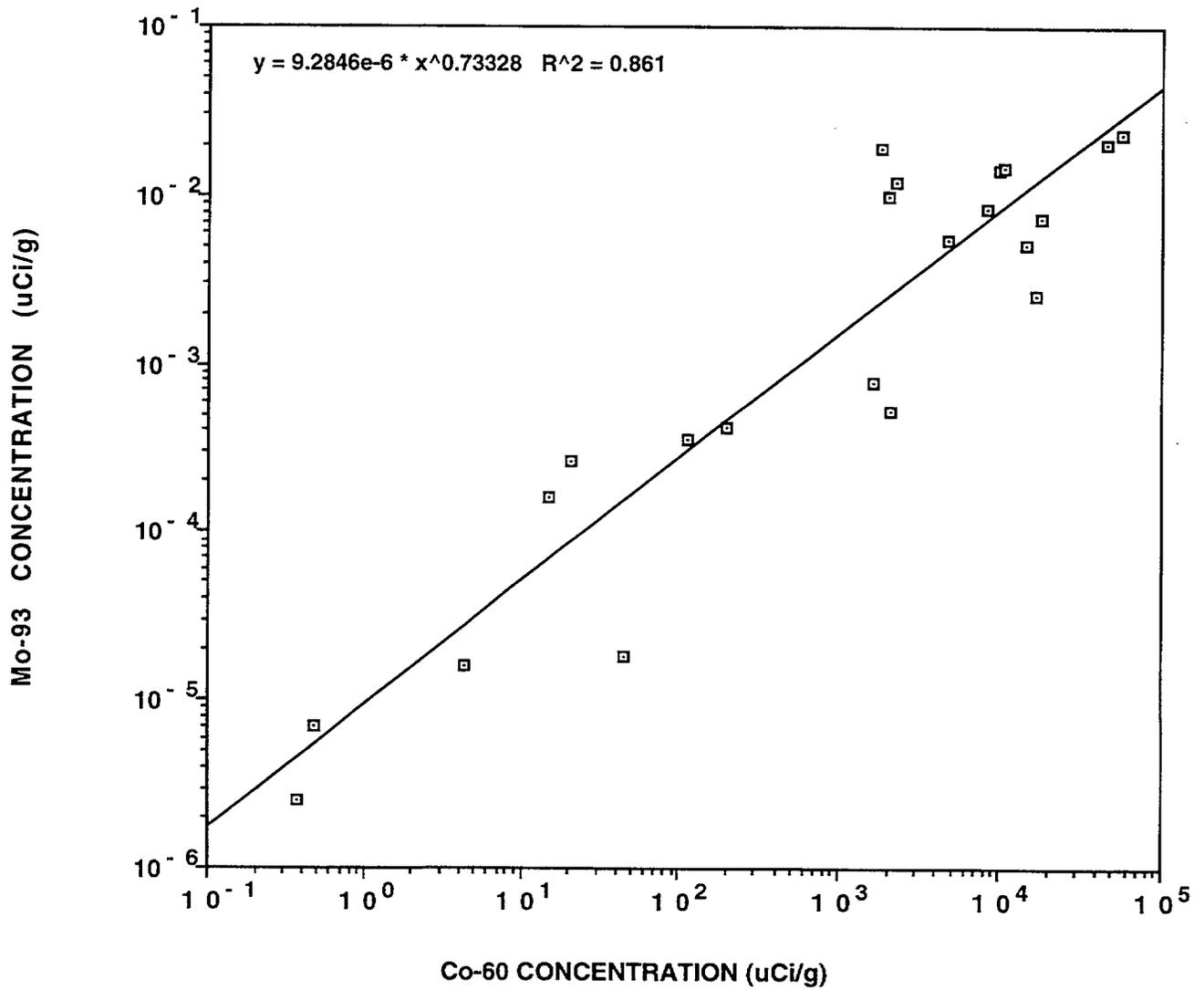
Figure 7.1   Correlation Between Mo-93 and Co-60 in Low-Level Wastes from Nuclear Power Stations

7.1.1.2 Niobium-93m

The NRC rule 10 CFR Part 61 specifically identifies ^{94}Nb as a reportable long-lived radionuclide in LLW. However, 10 CFR Part 61 does not mention ^{93m}Nb, despite the fact that its concentration is over two orders of magnitude higher than ^{94}Nb in neutron-activated metal waste. The reason 10 CFR Part 61 is more concerned about ^{94}Nb is because of its longer half-life (20,000 years) compared to ^{93m}Nb (half-life = 16.1 years), and the higher energy gamma-ray emissions of ^{94}Nb (871 and 703 keV). Niobium-93m decays by emission of a 30-keV gamma-ray which is essentially all internally converted. The predominant external radiation emitted by ^{93m}Nb is due to the 16.5-keV Nb x-rays. Previous calculations of ^{94}Nb and ^{93m}Nb in the neutron-activated shroud from a reference BWR estimated that the ^{93m}Nb/^{94}Nb ratio would be 0.09 (Oak, Holder, Kennedy, and Konzek 1980). However, more recent empirical measurements have shown that the average value of this ratio for irradiated stainless steel spent fuel assembly hardware is 158 (Robertson, Thomas, Wynhoff, and Hetzer 1991). Thus, the actual measured concentrations of ^{93m}Nb in neutron-activated stainless steel is 1800 times higher than previously calculated.

Table 7.2 lists the measured activity scaling factors for the ^{93m}Nb/^{60}Co ratio in samples measured in this study, plus data from NUREG/CR-6390 (Lepel, et al., 1995). The geometric mean of this scaling factor for twenty different activated metal samples and two samples of spent ion exchange resins was 6.91E-4. Figure 7.2 shows a reasonable correlation between ^{93m}Nb and ^{60}Co concentrations in the LLW materials listed in Table 7.2. Thus, a generic activity scaling factor for this radionuclide may be justified for nuclear power station LLW.

7.1.1.3 Silver-108m

Silver-108m is primarily produced in the Ag-Cd-In alloy used for neutron absorption in RCCA control rods from PWR stations. Silver-108m is generally not detectable in other types of LLW generated at nuclear power stations. As shown in Table 7.3 the ^{108m}Ag/^{60}Co activity scaling factors for all types of LLW except the RCCA control rods are "less-than" values ranging from <1.1E-2 to <3.4E-4. The Ag-

Cd-In alloy from the RCCA control rod measured in this study, together with earlier analyses published in NUREG/CR-6390 (Lepel, et al., 1995), show a rather consistent ^{108m}Ag/^{60}Co activity scaling factor averaging 8.45. As discussed in Section 5.1, the ^{108m}Ag is the most abundant radionuclide in this type of neutron activated material, and because it decays with the emission of several relatively high energy gamma rays it is quite easy to measure by direct gamma-ray spectrometry. Therefore, an activity scaling factor may not be necessary for this radionuclide because it can be measured directly.

7.1.1.4 Cadmium-113m

Cadmium-113m is likewise produced in the Ag-Cd-In alloy used in RCCA control rods. Table 7.4 lists the ^{113m}Cd/^{60}Co activity scaling factors for a variety of LLW from nuclear power stations. The scaling factors for non-RCCA type materials are low and range from <5.0E-5 to 1.8E-3. Even the scaling factors for the Ag-Cd-In alloy materials are quite variable, and range from 0.226 to 5.69. This large variability may be due to either large ranges in cobalt impurities in the alloy, and/or differences in the neutron capture cross section versus neutron energy for the two parent isotopes. In any event, there does not appear to be a useable generic activity scaling factor (relative to ^{60}Co) for this radionuclide based on the limited data base of measurements in LLW. A more useful scaling factor for the Ag-Cd-In alloy material appears to be the ^{113m}Cd/^{108m}Ag ratio, since the ^{108m}Ag can be measured easily by direct gamma-ray spectrometry in this material.

7.1.1.5 Tin-121m

Tin-121m was not detectable in any of the activated metal or spent resin samples measured in this study (see Table 7.5). For the five LLW sample types analyzed, an average ^{121m}Sn/^{60}Co activity scaling factor of <5.0E-5 was determined. However, because of the very low concentrations of ^{121m}Sn in LLW, the need for a generic activity scaling factor would be very limited.

Table 7.2 ^{93m}Nb/^{60}Co Scaling Factors for Low-Level Waste

| ID No. | Sample | Material | Concentration (µCi/g)[a] | | Scaling Factor |
			^{93m}Nb	^{60}Co	^{93m}Nb/^{60}Co
DER-1	Duane Arnold CRB[b]	SS	45.6	1.08E-4	4.22E-3
DER-1Z	"	SS	73.6	8.37E-3	8.75E-3
DER-2	"	SS	1.32	7.87E-3	1.68E-4
DER-2Z	"	SS	3.17	4.79E-3	6.62E-4
DER-3	"	SS	2.94E-2	2.03E-2	1.44E-4
DER-3Z	"	SS	4.74E-2	1.14E-2	4.16E-4
DER-4(out)	Point Beach BPRA[c]	SS	2.31	1.49E-4	1.55E-4
DER-4(in)	"	SS	5.13	1.80E-3	2.85E-3
DER-5(out)	"	SS	2.86	1.79E-4	1.60E-4
DER-5(in)	"	SS	6.26	2.20E-3	2.85E-3
DER-6(out)	"	SS	2.84	1.70E-4	1.67E-4
DER-6(in)	"	SS	5.66	2.01E-3	2.82E-3
DER-10A	Point Beach RCCA[d]	SS	41.4	4.54E-4	9.12E-4
DER-10B	"	SS	24.0	5.69E-4	4.22E-4
DER-8	"	SS	1.37	9.85E-3	1.39E-4
#39	Peach Bottom LPRM[e]	SS	2.40E-4	0.371	6.47E-4
#43	Duane Arnold CRB	SS	0.503	2.12E-3	2.37E-4
#40	Peach Bottom CRB	SS	2.20E-3	0.484	4.55E-3
#41	Point Beach BPRA (Spring)	Inconel	0.256	15.2	1.68E-2

Table 7.2 (continued)

| ID No. | Sample | Material | Concentration (µCi/g)[a] | | Scaling Factor |
			^{93m}Nb	^{60}Co	^{93m}Nb/^{60}Co
#42	Point Beach RCCA	Ag-Cd-In	4.56E-3	45.0	1.01E-4
#23	Cyrstal River RWCU Resin [f]	Resin	4.20E-3	4.36	9.63E-4
#22	WNP-2 Resin	Resin	4.28E-3	20.8	2.06E-4
				Mean *	2.20E-3
				Standard Deviation	3.90E-3
				Geometric Mean **	6.91E-4

(a) Concentrations decay-corrected to 5 years after discharge of components or materials from the reactor. It was necessary to sandardize the decay time after discharge from the reactors because some of the materials were quite old and the ^{60}Co had undergone substantial radioactive decay.
(b) CRB = Control Rod Blade
(c) BPRA = Burnable Poison Rod Assembly
(d) RCCA = Rod Cluster Control Assembly
(e) LPRM = Low Power Range Monitor
(f) RWCU = Reactor Water Clean-Up

Note: All DER sample data from NUREG/CR-6390 (Lepel, et al., 1995)

   * Arithmetic mean of all 22 samples

   ** Geometric mean of all 22 samples

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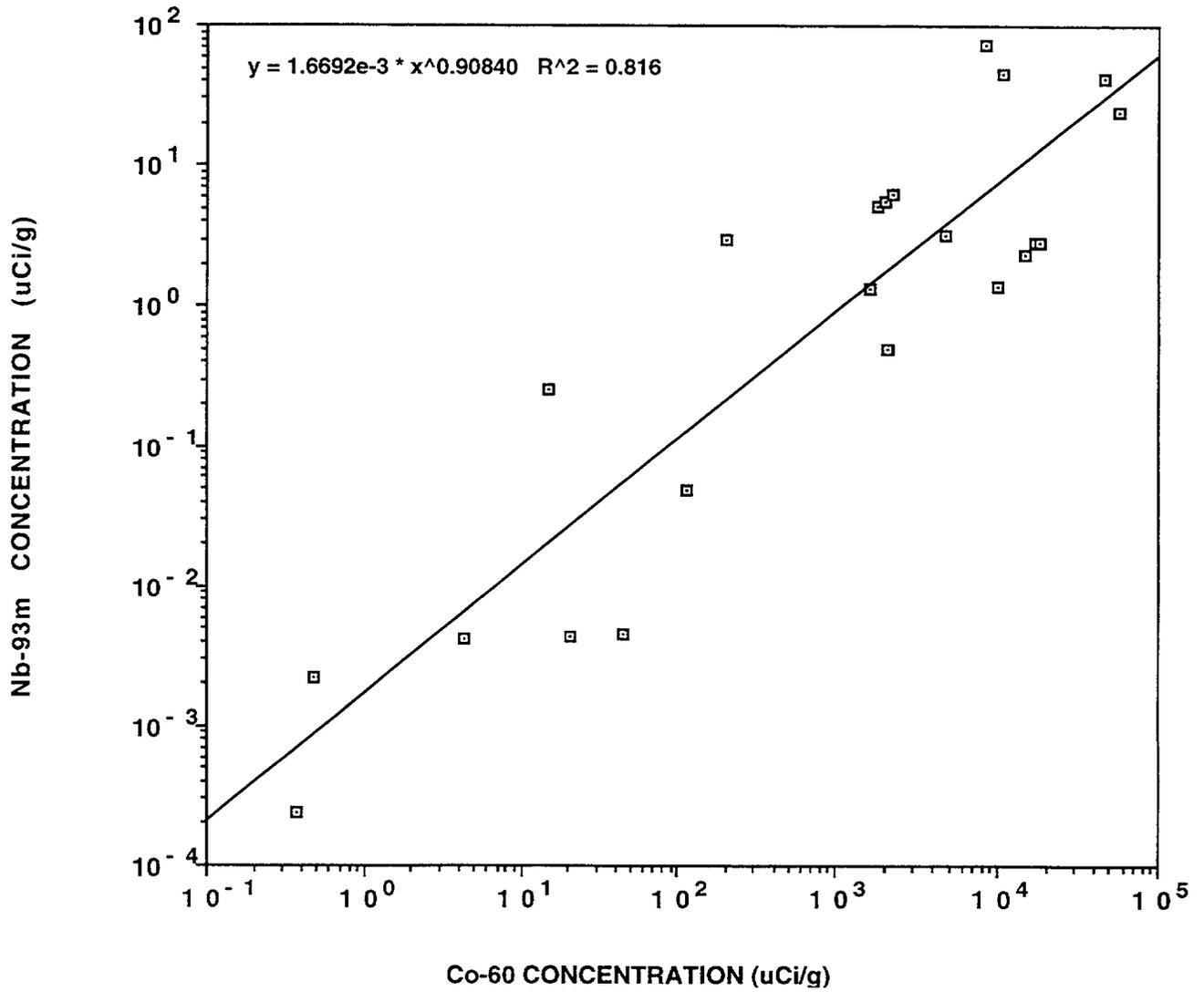
Figure 7.2   Correlation Between Nb-93m and Co-60 in Low-Level Wastes from Nuclear Power Stations

Table 7.3 Silver-108m and ^{60}Co Concentrations in Selected LLW Samples

| Sample | Material | Source | Concentration(μCi/g)* | | Scaling Factor |
			^{108m}Ag	^{60}Co	^{108m}Ag/^{60}Co
#39	stainless steel	LPRM Cladding[a] Peach Bottom	<2.4E-4	3.71E-1	<6.5E-4
#40	stainless steel	Control Rod Blade Peach Bottom	<6.5E-4	4.84E-1	<1.34E-3
#43	stainless steel	Control Rod Blade Duane Arnold	<1.4	2.12E-3	<6.6E-4
#41	Inconel spring	BPRA Control Rod[b] Point Beach	<5.1E-3	1.52E-1	<3.4E-4
#42	Ag-Cd-In Alloy	RCCA Control Rod[c] Point Beach	6.37 ± 0.19E2	4.50E-1	14.2
DER-7	Ag-Cd-In Alloy	RCCA Control Rod Point Beach	5.44E-3	5.75E-4	9.46
DER-8	Ag-Cd-In Alloy	RCCA Control Rod Point Beach	1.12E-2	1.46E-3	7.67
DER-9	Ag-Cd-In Alloy	RCCA Control Rod Point Beach	1.11	1.06E-1	10.5
DER-10A	Ag-Cd-In Alloy	RCCA Control Rod Point Beach	2.14E-4	2.52E-3	8.49
DER-10B	Ag-Cd-In Alloy	RCCA Control Rod Point Beach	2.73E-4	4.46E-3	6.12
#23	ion exchange resin	RWCU Resin[d] Crystal River	<5.0E-2	4.36E-0	<1.1E-2
#22	ion exchange resin	EDRFDR + RWCU[e] WNP-2	<1.3E-2	2.08E-1	<6.3E-4

* Concentrations decay corrected to 5 years after discharge of components or materials from reactors
(a) LPRM = Low Power Range Monitor
(b) BPRA = Burnable Poison Rod Assembly
(c) RCCA = Rod Cluster Control Assembly
(d) RWCU = Reactor Water clean-Up
(e) EDRFDR = Equipment Drain Radioactive/Floor Drain Radioactive

Table 7.4 Cadmium-113m and ^{60}Co Concentrations in Selected LLW Samples

Sample	Material	Source	Concentration(μCi/g)*		Scaling Factor
			^{113m}Cd	^{60}Co	^{113m}Cd/^{60}Co
#39	stainless steel	LPRM Cladding[a] Peach Bottom	<1.2E-4	3.71E-1	<3.3E-4
#43	stainless steel	Control Rod Blade Duane Arnold	1.06E-1	2.12E-3	5.0E-5
#41	Inconel spring	BPRA Control Rod[b] Point Beach	2.76E-2	1.52E-1	1.8E-3
#42	Ag-Cd-In Alloy	RCCA Control Rod[c] Point Beach	28.0 ± 0.1	4.5E-1	6.23E-1
DER-9	Ag-Cd-In Alloy	RCCA Control Rod[c] Point Beach	0.603	1.06E-1	5.69
DER-10A	Ag-Cd-In Alloy	RCCA Control Rod[c] Point Beach	577	2.55E-3	0.226
DER-10B	Ag-Cd-In Alloy	RCCA Control Rod[c] Point Beach	1020	4.51E-3	0.226
#23	ion exchange resin	RWCU Resin[d] Crystal River	4.9 ± 1.0E-3	4.36	1.1E-3
#22	ion exchange resin	EDRFDR + RWCU[e] WNP-2	1.54 ± 0.5E-2	2.08E-1	7.40E-4

*   Concentrations decay corrected to 5 years after discharge of components or materials from reactors

(a)   LPRM = Low Power Range Monitor
(b)   BPRA = Burnable Poison Rod Assembly
(c)   RCCA = Rod Cluster Control Assembly
(d)   RWCU = Reactor Water Clean-Up
(e)   EDRFDR = Equipment Drain Radioactive/Floor Drain Radioactive

7.1.2 Chlorine-36

Chlorine-36 was detectable in only the spent ion exchange resin samples from the two PWR nuclear power stations (see Table 7.6). The average $^{36}Cl/^{60}Co$ activity scaling factor for these two samples was 2.65E-4. The $^{36}Cl/^{137}Cs$ activity scaling factor ranged from 1.43E-6 to 1.02E-5 and averaged 5.8E-6. This value is in good agreement with the limited data reported for spent primary resin samples from Swiss PWR and BWR nuclear power stations (Liu, et al., 1991). Although the ^{36}Cl concentrations in spent primary resins is quite low, its very long half-life, high environmental mobility, and relatively high ingestion dose conversion factor may require that a more detailed radiological performance assessment for its disposal in LLW be conducted.

7.1.3 Beryllium-10

Beryllium-10 is produced in LLW from nuclear power stations as a by-product from neutron activation of ^{10}B present in control rods (as B_4C and borosilicate glass) and in primary coolant (as soluble borate). Therefore, ^{10}Be is a significant contaminant in spent control rods and primary coolant demineralization resins. The concentration of soluble boron in PWR primary coolant can range from 10 to 2300 ppm B depending on the burnup in the fuel cycle. Therefore, the production of ^{10}Be from neutron activation of ^{10}B can vary by a factor of up to 230, and ^{10}Be concentrations in primary coolant (and primary demineralization resins) would also be expected to be quite variable.

Table 7.7 lists the $^{10}Be/^{60}Co$ activity scaling factors for activated metal and spent resin LLW samples. Beryllium-10 concentrations in the activated metal samples were non-detectable, except for a trace amount in the Inconel speciman (Sample #41). Of the resin samples, only the Diablo Canyon sample (#2-2) contained detectable ^{10}Be. As shown in Figure 5.6, the ^{10}Be in this spent resin will be the third most abundant radionuclide (behind ^{14}C and ^{59}Ni) after a disposal period of about 600 years. The $^{10}Be/^{60}Co$ activity scaling factor for the Diablo Canyon resin sample was 9.45E-4. However, this scaling factor would be expected to be quite variable depending on the burnup in the fuel cycle, and should not be

considered representative of a generic scaling factor for spent resin LLW.

The $^{10}Be/^{60}Co$ scaling factors for the boron carbide present in the two samples of the spent Duane Arnold control rod blade were less variable and averaged 5.38E-3. The scaling factor for the borosilicate glass in the BPRA rod from Point Beach was 5.31E-4. These scaling factors are probably fairly representative of these materials, and may be useful for estimating ^{10}Be concentrations in these materials by gamma counting for ^{60}Co. These are the only known measured $^{10}Be/^{60}Co$ scaling factors in existence.

Because of the very long half-life of ^{10}Be (1.6E6 years), together with its relatively low soil adsorption in sandy types of soil and its relatively high ingestion dose conversion factor, it is recommended that further radiological assessment be conducted to better predict its potential radiation dose to man from disposal in LLW.

7.2 Review of Scaling Factors for ^{14}C, ^{99}Tc, and ^{129}I for Low-Level Waste

Recent assessments of shipping manifest data for LLW being disposed from commercial nuclear power stations have shown that the concentrations of ^{129}I and ^{99}Tc have been conservatively overestimated by several orders of magnitude. Anomalies in the ^{14}C data base were also observed. Bhattacharyya, Janati, and Shearer (1987) were the first to point out that the nuclear power industry's radionuclide source term data base is overly conservative with respect to the concentrations of ^{129}I in LLW generated by nuclear power stations. The shipping manifests for LLW generated at nuclear power stations normally report "less-than" values for ^{129}I and ^{99}Tc which are supplied by service analytical laboratories who perform the required analyses for the utilities to meet 10 CFR Part 61 requirements for waste classification. The reported "less-than" values are simply the lower-limit-of-detection of the radiometric methods used by the analytical laboratories. Iodine-129 is a low-energy beta and photon emitter, and ^{99}Tc and ^{14}C are

Table 7.5 Tin-121m and [60]Co Concentrations in Selected LLW Samples

| Sample | Material | Source | Concentration(μCi/g)* | | Scaling Factor |
			^{121m}Sn	^{60}Co	$^{121m}Sn/^{60}Co$
#40	stainless steel	Control Rod Blade Peach Bottom	<2.1E-4	4.84E-1	<4.3E-4
#41	Inconel spring	BPRA Control Rod[a] Point Beach	<9.9E-5	1.52E-1	<6.5E-6
#42	Ag-Cd-In Alloy	RCCA Control Rod[b] Point Beach	<1.5E-3	4.50E-1	<3.3E-5
#23	ion exchange resin	RWCU Resin[c] Crystal River	<3.9E-4	4.36E-0	<8.9E-5
#22	ion exchange resin	EDRFDR + RWCU[d] WNP-2	<5.2E-3	2.08E-1	<2.5E-4

*   Concentrations decay corrected to 5 years after discharge of components or materials from reactors

(a)   BPRA = Burnable Poison Rod Assembly
(b)   RCCA = Rod Cluster Control Assembly
(c)   RWCU = Reactor Water Clean-Up
(d)   EDRFDR = Equipment Drain Radioactive/Floor Drain Radioactive

Table 7.6 Chlorine-36 and ^{60}Co Concentrations in Selected LLW Samples

| Sample | Material | Source | Concentration(μCi/g)* | | Scaling Factor |
			^{36}Cl	^{60}Co	^{36}Cl/^{60}Co
2-2	ion exchange resin	RWCU resin[a] Diablo Canyon	9.3 ± 2.2E-5	8.70	1.1E-5
#23	ion exchange resin	RWCU resin Crystal River	2.3 ± 1.1E-3	4.36	5.3E-4
#22	ion exchange resin	EDRFDR + RWCU[b] WNP-2	<7.9E-4	20.8	<3.8E-5
#39	stainless steel	LPRM Cladding[c] Peach Bottom	<3.7E-5	3.71E-1	<9.9E-5
#40	stainless steel	Control Rod Blade Peach Bottom	<7.2E-5	4.84E-1	<1.5E-4
#43	stainless steel	Control Rod Blade Duane Arnold	<1.8E-3	2.23E-3	<8.1E-7
#41	Inconel spring	BPRA Control Rod[d] Point Beach	3.9 ± 0.9E-4	1.52E-1	2.6E-5

*   Concentrations decay correted to 5 years after discharge of components or materials from reactors

(a) RWCU = Reactor Water Clean-Up
(b) EDRFDR = Equipment Drain Radioactive/Floor Drain Radioactive
(c) LPRM = Low Power Range Monitor
(d) Burnable Poison Rod Assembly

Table 7.7 Beryllium-10 and ^{60}Co Concentrations in Selected LLW Samples

| Sample | Material | Source | Concentration(μCi/g)* | | Scaling Factor |
			^{10}Be	^{60}Co	^{10}Be/^{60}Co
DER-1	boron carbide	Spent BWR Control Rod Blade Duane Arnold	3.68 ± 0.04E-2	10.2	3.61E-3
DER-2	boron carbide	Spent BWR Control Rod Blade Duane Arnold	3.91 ± 0.04E-2	5.47	7.15E-3
DER-4	borosilicate glass	Spent PWR BPRA Rod[a] Point Beach	2.72 ± 0.08E-3	5.12	5.31E-4
2-2	ion exchange resin	RWCU Resin[b] Diablo Canyon	8.22 ± 0.36E-3	8.70	9.45E-4
#23	ion exchange resin	RWCU Resin Crystal River	<1.08E-4	4.36	<2.5E-5
#22	ion exchange resin	EDRFDR + RWCU[c] WNP-2	<7.9E-4	20.8	<3.8E-5
#39	stainless steel	LPRM Cladding[d] Peach Bottom	<5.3E-5	3.71E-1	<1.4E-4
#40	stainless steel	Control Rod Blade Peach Bottom	<8.2E-5	4.84E-1	<1.7E-4
#43	stainless steel	Control Rod Blade Duane Arnold	<2.2E-3	2.23E-3	<9.9E-7
#41	Inconel spring	BPRA Control Rod Point Beach	1.20 ± 0.05E-4	15.2	7.9E-6
#42	Ag-Cd-In Alloy	RCCA Control Rod[e] Point Beach	<1.6E-4	45.0	<3.6E-6

* Concentrations decay corrected to 5 years after discharge of components or materials from reactors
(a) BPRA + Burnable Poison Rod Assembly
(b) RWCU = Reactor Water Clean-Up
(c) EDRFDR = Equipment Drain Radioactive/Floor Drain Radioactive
(d) LPRM = Low Power Range Monitor
(e) RCCA = Rod Cluster Control Assembly

pure beta emitters. Their analyses require radiochemical purification followed by either beta or low-energy photon counting.

The usual practice by the nuclear power industry is to send a limited number of selected LLW samples, on an annual or semi-annual basis, to the service analytical laboratories for comprehensive 10 CFR Part 61 radionuclide analyses. Then each nuclear power station generates an updated, station-specific data base from which activity scaling factors for the difficult-to-measure radionuclides are calculated relative to easily measured gamma-emitting radionuclides (i.e., ^{137}Cs and ^{60}Co) usually present in the LLW. Then, the concentrations of the difficult-to-measure radionuclides can be estimated in batches of LLW by measuring the gamma-emitting radionuclides and applying the activity scaling factors developed for various waste types at each station. This procedure is entirely adequate for waste classification, and the reported "less than" concentrations are generally orders of magnitude below the least-restrictive Class A waste category. However, the true concentrations of ^{129}I and ^{99}Tc in the LLW are generally several orders of magnitude below the "less-than" values reported by the analytical laboratories.

The problem associated with this methodology came later, when performance assessment modeling for future LLW disposal sites, using the highly conservative industry data base consisting primarily of "less-than" values for ^{129}I in LLW, indicated that the ^{129}I releases from the site would exceed the dose limits specified by 10 CFR Part 61, and thereby limit the quantities of LLW that could be disposed at a shallow-land burial facility. The obvious need of the nuclear power industry is to determine the actual concentrations of ^{129}I and ^{99}Tc in LLW by an analytical method, such as mass spectrometry, which possesses adequate sensitivity to measure the actual concentrations of these nuclides. Using a more accurate data base in performance assessment modeling would eliminate these two radionuclides as major contributors to the offsite dose from a LLW disposal facility.

7.2.1 Recent Mass Spectrometric Measurements of ^{129}I and ^{99}Tc in LLW

During the past several years PNNL has conducted a number of programs for EPRI, NRC, and other clients (Vance and Associates, as well as a number of nuclear utilities) during which a variety of LLW samples from commercial nuclear power stations have been analyzed for ^{129}I and ^{99}Tc by extremely sensitive mass spectrometric methods. In addition, the gamma-emitting radionuclides that are used for developing activity scaling factors were measured in the same samples, i.e., ^{137}Cs and ^{60}Co. These measurements have provided the most accurate data base to date of these activity scaling factors. Because of the large differences between the two data bases, the dissemination of the accurate mass spectrometric data would benefit the nuclear utilities, state and federal regulators, performance assessment modelers, radioactive waste managers, and LLW disposal facility operators.

7.2.1.1 Sampling

A variety of LLW sample types from a number of commercial nuclear power stations were collected for analysis over the past several years. Because the reactor primary coolant is the main source of ^{129}I, ^{99}Tc, and other fission and activation products in LLW, a concerted effort was made to characterize the concentrations of these radionuclides in mixed-bed ion exchange resins used for demineralization of the primary coolant. To more carefully track the behavior of these radionuclides on mixed-bed ion exchange resin, scaled-down versions of the reactor primary coolant demineralizer systems were constructed, installed, and operated at PWR and BWR stations to sample the primary coolant.

For PWR stations, the scaled-down primary purification demineralizer systems were placed in-line in the primary coolant sampling line, and primary coolant was passed through the ion exchange resin column for periods ranging from several days to up to six weeks to simulate the cleanup operations and resin loading at a commercial PWR station. The test column consisted of a 40-cm long by 2.5-cm inside diameter Plexiglass tube with stainless steel

screens placed on each end to contain the resin. The column was filled with about 30 cm of the standard mixed-bed resin routinely used at each station for cleanup of the primary coolant. The primary coolant flow rate through the column was scaled-down proportionally to the size of the column and typically was about 80 mL/min. Columns were installed at a number of stations to obtain an adequate data base for determining the concentrations and distributions of the isotopes on the resin and for computing reliable activity scaling factors. After processing the primary coolant, the column was disconnected and carefully packaged for shipping to PNNL for radiochemical and mass spectrometric analysis of the resin samples.

For BWR stations, the typical powdered resin used for primary coolant cleanup was utilized in a scaled-down, in-line filter assembly to simulate the coolant cleanup process used at BWR stations. A 2-cm diameter Millipore stainless steel in-line filter holder was loaded with about 1.2 g of powdered resin to form a 0.6-cm thick bed, and reactor coolant was pumped through the resin bed at a flow rate of 42 mL/min for 48 hours. The resin holder was then disconnected, packaged, and shipped to PNNL for radionuclide analysis of the resin.

In addition to the test resin samples, a variety of LLW samples were obtained from nuclear power stations, including primary and secondary resins, primary coolant water, dry active waste (DAW), primary coolant purification filters, charcoal, soil, and spent oil, for a total of 43 samples.

7.2.1.2 Radiochemical and Mass Spectrometric Analyses for ^{129}I and ^{99}Tc in LLW

The samples were first homogenized and appropriate aliquots taken for direct gamma-ray spectrometric analyses to measure the gamma-emitting radionuclides. Then the gamma-counted aliquots were subjected to destructive radiochemical analyses of ^{129}I and ^{99}Tc, and quantified by two mass spectrometric methods.

The ^{129}I was separated from the sample matrix by controlled combustion in oxygen, trapping the volatilized iodine on charcoal, and further purifying

the iodine prior to loading the iodine (as silver iodide) on a lanthanum hexaboride-coated rhenium filament for thermal emission mass spectrometric analysis (Strebin, Brauer, Kaye, Rapids, and Stoffels 1988). The detection limit afforded by this method is about 4 x 10^{-13} μCi of ^{129}I, which provides adequate sensitivity to accurately measure ^{129}I in essentially any type of LLW sample from the nuclear power stations.

The ^{99}Tc was separated from the sample matrix by leaching with hot 10 $\underline{M}$ nitric acid, evaporating the acid to near dryness, dissolving the residue in 0.01 $\underline{M}$ nitric acid, and purifying the Tc by an ion exchange procedure (Robertson, Smith, Koppenaal 1990). The final separated Tc was dissolved in 1.0 mL of 1 $\underline{M}$ nitric acid which was then submitted for ^{99}Tc analysis by inductively coupled plasma mass spectrometry (Smith, Wyse, and Koppenaal 1992). This method provided a detection limit of about 1 x 10^{-8} μCi of ^{99}Tc.

7.2.1.3 Results of Mass Spectrometric Analyses of ^{129}I and ^{99}Tc in LLW

The results of the gamma-spectrometric and mass spectrometric analyses of the test resin samples and the LLW samples are presented in Table 7.8, which lists the concentrations of ^{129}I, ^{99}Tc, and the gamma-emitters ^{137}Cs and ^{60}Co that are used for developing activity scaling factors. Also listed are the computed activity scaling factors for ^{129}I and ^{99}Tc relative to the gamma-emitters. Table 7.8 was compiled frommeasurements made during this study, from measurements published in Vance, et al. 1992, in Robertson, et al. 1990, 1997, and from previously unpublished measurements made at PNNL.

Because of the diverse nature of the LLW samples from a number of PWR and BWR stations which were analyzed, the concentrations of these nuclides ranged over four to seven orders of magnitude. The highest concentrations were generally observed in primary demineralization resins which remove these radionuclides from the reactor coolant, and the concentrations of ^{129}I and ^{99}Tc varied by about three orders of magnitude in these resins. The primary coolant cleanup filters contained the highest concentrations of ^{60}Co and other activation products, but not necessarily the soluble fission products, such

as ^{129}I and ^{99}Tc.

7.2.1.4 Correlation of ^{129}I and ^{99}Tc with Gamma-Emitting Radionuclides

The radionuclide concentrations generated in the reactor primary coolant (the source-term for LLW radionuclides) are dependant on a number of factors, including the amount of tramp uranium on the fuel element surfaces, the degree of fuel element integrity, the elemental composition of the materials of construction of the primary loop system, the corrosion rates of primary loop materials, and the reactor coolant chemistry. Because these factors can be highly variable from station to station, the relative concentrations of fission and activation products in the primary coolant can also vary significantly.

Iodine-129 and ^{137}Cs are strictly fission products which are relatively soluble in the reactor primary coolant, and ^{60}Co is strictly an activation product of limited solubility. For this reason, and despite the fact that ^{129}I is present in reactor coolant as an anion and ^{137}Cs is present as a cation, ^{129}I is usually correlated with ^{137}Cs to provide activity scaling factors for estimating the quantities of ^{129}I from the ^{137}Cs concentrations in LLW measured by gamma-ray spectrometry.

In addition to being a fission product, ^{99}Tc is also produced by thermal neutron activation of molybdenum, and enters the primary coolant by corrosion/dissolution of the molybdenum-containing construction materials (e.g., stainless steel, some Inconel and titanium alloys) present in the primary coolant system. At some nuclear power stations the quantities of ^{99}Tc produced by neutron activation of molybdenum is quite significant relative to fission product ^{99}Tc.

Figures 7.3a and 7.3b show the correlations of ^{129}I with ^{137}Cs and with ^{60}Co for all resin and LLW samples. These two radionuclides are the most commonly used gamma-emitters utilized for computing scaling factors. As the scatter diagrams show, the correlation between ^{129}I and ^{137}Cs is quite good, even for diverse sample types having radionuclide concentrations ranging over eight orders of magnitude. The regression analysis for this data set gave an R^2 value of 0.852. Thus, the use of

^{129}I/^{137}Cs scaling factors for all types of LLW appears to be a reasonable method for estimating the concentrations of ^{129}I. An assessment of the correlations with respect to sample type, reactor station type (PWR and BWR), and sample activity levels showed no definite trends, except for the observation that the ^{129}I and ^{137}Cs correlations were much better for PWR stations compared to BWR stations. The reason for this anomaly may be due to the fact that in BWR stations approximately two-thirds of the reactor coolant iodine can be transported by the steam to the condensate resin while most of the cesium would be expected to be removed by the primary demineralization system (Vance, Helmholz, and Sutherland 1988). As might be expected, the correlation of ^{129}I with ^{60}Co was quite poor due to their different production modes and physico-chemical behaviors in reactor coolant.

Figures 7.4a and 7.4b show the correlations of ^{99}Tc with ^{60}Co and ^{137}Cs. These data show a reasonable correlation of ^{99}Tc with ^{60}Co (R^2 value of 0.631), but essentially no correlation with ^{137}Cs. These observations are not entirely unexpected, and suggest that the most significant production mode for ^{99}Tc at many nuclear power stations may be by neutron activation of molybdenum. Technetium has normally been assumed to behave as the soluble Tc(VII) pertechnetate anion in reactor coolant. However, this assumption may not be entirely correct, particularly in view of its apparent correlation with ^{60}Co, which suggests that much of the technetium may be presence in reactor coolant in a less-soluble reduced oxidation state. For those nuclear power stations experiencing a relatively high rate of fuel cladding failures, the ^{99}Tc/^{137}Cs scaling factor would be expected to show less variability.

7.2.1.5 Comparison of PNNL and Industry Scaling Factors

The activity scaling factors for ^{129}I and ^{99}Tc computed from the PNNL data base in which highly sensitive and selective mass spectrometric measurement techniques were utilized were much lower than the scaling factors developed from the nuclear power industry data base. The industry data bases contain LLW radionuclide concentrations and activity scaling factors for most of the nuclear power stations in the U. S., and have been published in the

Table 7.8 Radionuclide Concentrations and Activity Scaling Factors for LLW from Commercial Nuclear Power Stations

SAMPLE TYPE	ID NUMBER	SAMPLE DATE	I-129 Bq/g	Tc-99 Bq/g	Cs-137 Bq/g	Co-60 Bq/g	I-129/Cs-137	Tc-99/Cs-137	I-129/Co-60	Tc-99/Co-60
primary resin	PWR Sta. A	7-Dec-89	1.02E+01	1.51E+01	1.37E+08	3.07E+05	7.47E-08	1.10E-07	3.33E-05	4.90E-05
primary resin	PWR Sta. B	5-Nov-90	2.46E+00	9.77E-01	4.26E+07	5.51E+05	5.76E-08	2.29E-08	4.47E-06	1.78E-06
primary resin	PWR Sta. C	13-Feb-90	9.10E-03	1.55E-01	8.66E+04	6.77E+05	1.05E-07	1.79E-06	1.35E-08	2.29E-07
primary resin	PWR Sta. D	13-Feb-90	1.10E+00	2.80E-01	8.29E+06	3.23E+04	1.33E-07	3.38E-08	3.41E-05	8.67E-06
primary resin	PWR Sta. E	21-Jan-90	1.09E-01	6.36E-02	2.56E+06	6.96E+03	4.26E-08	2.48E-08	1.57E-05	9.15E-06
primary resin	PWR Sta. F	19-Aug-90	1.79E-01	1.62E-01	3.33E+05	7.66E+03	5.38E-07	4.85E-07	2.34E-05	2.11E-05
primary resin	PWR Sta. G	6-Jul-92	5.40E-03	2.33E-02	5.03E+04	5.40E+03	1.07E-07	4.63E-07	1.00E-06	4.32E-06
primary resin	PWR Sta. B	5-Feb-92	3.25E-02	9.62E-03	2.70E+06	2.33E+03	1.20E-08	3.56E-09	1.40E-05	4.13E-06
primary resin	PWR Sta. B	30-Jan-92	2.01E-02	1.78E-02	2.18E+06	1.41E+03	9.19E-09	8.14E-09	1.43E-05	1.26E-05
primary resin	PWR Sta. C	15-Jan-92	1.47E-02	1.96E-02	3.30E+06	5.40E+04	4.44E-09	5.94E-09	2.71E-07	3.63E-07
primary resin	PWR Sta. D	15-Apr-92	7.55E-02	1.70E-02	4.92E+04	3.04E+04	1.53E-06	3.46E-07	2.48E-06	5.60E-07
primary resin	PWR Sta. H	9-Nov-90	7.81E-03	3.66E-02	6.81E+05	6.55E+04	1.15E-08	5.38E-08	1.19E-07	5.59E-07
primary resin	PWR Sta. I	29-Nov-90	3.52E-02	7.03E-02	9.07E+04	4.44E+04	3.89E-07	7.76E-07	7.93E-07	1.58E-06
primary resin	PWR Sta. J	14-Dec-90	1.49E-02	4.44E-02	3.92E+06	5.66E+04	3.80E-09	1.13E-08	2.63E-07	7.84E-07
primary resin	PWR Sta. K	10-Apr-96	1.18E+00	2.66E-01	2.37E+07	6.07E+06	4.98E-08	1.12E-08	1.95E-07	4.39E-08
primary resin	PWR Sta. K	1-Jan-96	4.26E-03	5.92E+00	1.48E+04	6.77E+06	2.88E-07	4.00E-04	6.28E-10	8.74E-07
primary resin	PWR Sta. D	22-Jan-86	3.32E-02	0.00E+00	6.51E+06	5.07E+05	5.09E-09		6.54E-08	
primary resin	BWR Sta. 1	12-Apr-90	1.30E-01	1.98E+01	6.59E+05	2.21E+06	1.97E-07	3.01E-05	5.85E-08	8.95E-06
primary resin	BWR Sta. 2	21-Mar-90	3.64E-01	1.49E+01	1.75E+06	1.45E+07	2.08E-07	8.54E-06	2.51E-08	1.03E-06
primary resin	BWR Sta. 3	26-Feb-90	7.40E-02	1.31E+00	1.80E+04	3.16E+06	4.11E-06	7.27E-05	2.34E-08	4.14E-07
primary resin	BWR Sta. 4	26-Feb-90	7.40E-02	1.11E+00	1.44E+03	3.41E+06	5.13E-05	7.72E-04	2.17E-08	3.27E-07
primary resin	BWR Sta. 5	1-Jul-92	2.01E-04	4.44E-01	8.70E+02	4.92E+05	2.31E-07	5.11E-04	4.08E-10	9.02E-07
primary resin	BWR Sta. 6	24-Jan-92	2.80E-04	1.86E+01	1.04E+03	1.03E+06	2.70E-07	1.80E-02	2.72E-10	1.81E-05
primary resin	BWR Sta. 7	13-Sep-90	4.81E-04	9.18E+00	1.41E+03	1.09E+06	3.42E-07	6.53E-03	4.42E-10	8.44E-06
primary resin	BWR Sta. 8	26-Oct-90	3.24E-04	2.61E+00	1.55E+03	1.91E+06	2.08E-07	1.68E-03	1.69E-10	1.36E-06
primary resin	BWR Sta. 2	22-Jan-92	3.19E-03	3.07E+00	1.26E+04	5.07E+06	2.53E-07	2.44E-04	6.28E-10	6.06E-07
primary resin	BWR Sta. 5	6-Jul-92	3.32E-04	2.81E-01	8.51E+03	7.40E+06	3.90E-08	3.30E-05	4.48E-11	3.80E-08
beborating demin. resin	PWR Sta. K	1-Jan-96	4.77E-04	4.81E+00	5.55E+03	1.16E+07	8.60E-08	8.67E-04	4.12E-11	4.15E-07
CVCS mixed demin. resin	PWR Sta. K	1-Jan-96	4.26E-03	5.92E+00	1.48E+04	6.73E+06	2.88E-07	4.00E-04	6.32E-10	8.79E-07
dry active waste	PWR Sta. L	12-Jun-09	1.23E-04	0.00E+00	1.45E+03	6.25E+03	8.52E-08		1.97E-08	
dry active waste	PWR Sta. M	12-Jun-09	1.46E-04	0.00E+00	1.24E+03	3.89E+02	1.17E-07		3.75E-07	
dry active waste	PWR Sta. C	12-Jun-09	1.15E-04	0.00E+00	2.29E+03	3.02E+03	5.01E-08		3.80E-08	
dry active waste	BWR Sta. 9	12-Jun-09	3.40E-03	0.00E+00	3.18E+03	5.92E+03	1.07E-06		5.74E-07	
dry active waste	BWR Sta. 10	12-Jun-09	6.66E-05	0.00E+00	8.84E+01	1.17E+03	7.53E-07		5.71E-08	
CVCS Filter	PWR Sta. D	12-Jun-09	5.55E-02	0.00E+00	1.97E+06	9.36E+08	2.82E-08		5.93E-11	
RCS letdown filter	PWR Sta. K	12-Apr-96	1.11E-02	1.11E+00	1.26E+05	4.40E+07	8.85E-08	8.82E-06	2.52E-10	2.51E-08
RF water purif. filter	PWR Sta. K	25-Apr-96	1.96E-03	8.14E+00	1.04E+05	9.62E+06	1.89E-08	7.86E-05	2.03E-10	8.46E-07
CCS filter	PWR Sta. K	25-May-95	7.55E-04	5.92E+01	9.25E+02	8.58E+07	8.16E-07	6.40E-02	8.79E-12	6.90E-07
charcoal	PWR Sta. C	12-Jun-09	3.89E-03		1.10E+05	2.09E+06	3.52E-08		1.86E-09	
secondary mixed resin	PWR Sta. N	12-Jun-09	1.22E-04		1.10E+03	6.99E+03	1.11E-07		1.74E-08	
soil	BWR Sta. 11	12-Jun-09	2.81E-06		1.38E+01	1.20E+01	2.03E-07		2.34E-07	
spent lubricating oil	BWR Sta. 10	12-Jun-09	3.25E-04		2.06E+03	1.81E+03	1.58E-07		1.80E-07	
reactor coolant	PWR Sta. C	26-May-88	4.18E-07		1.41E+01	3.62E+00	2.97E-08		1.15E-07	
RWCU primary resin	BWR Sta. 2	20-Apr-93	6.07E-02		2.28E+05		2.74E-07			
primary demin. resin	PWR Sta. D	10-Nov-92	2.41E+01		8.25E+07		2.92E-07			
		geometric mean					1.20E-07	5.23E-06	3.76E-08	1.67E-06
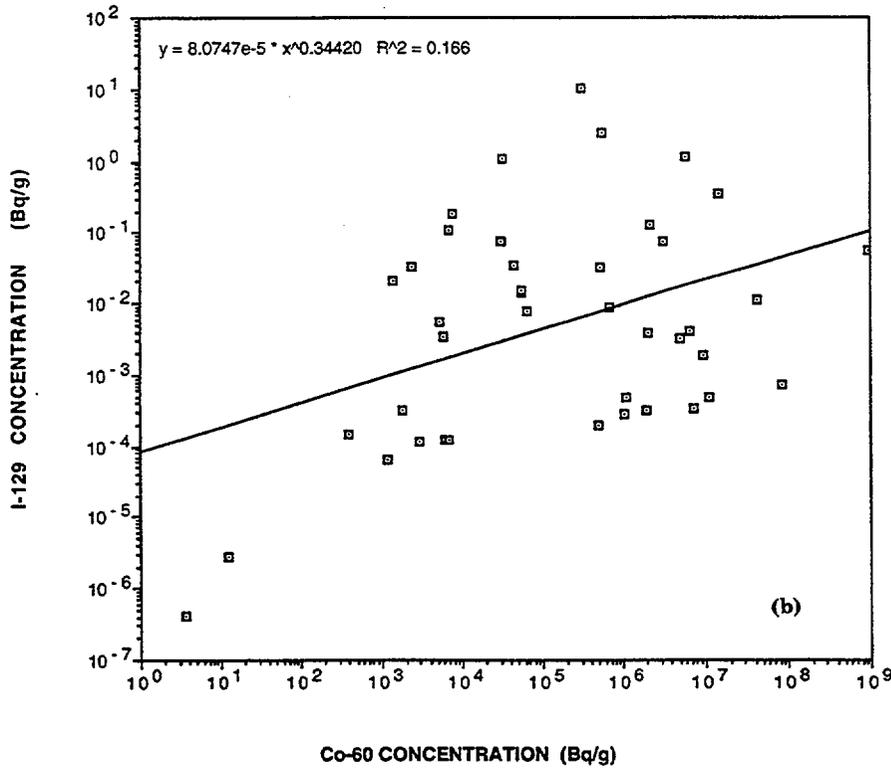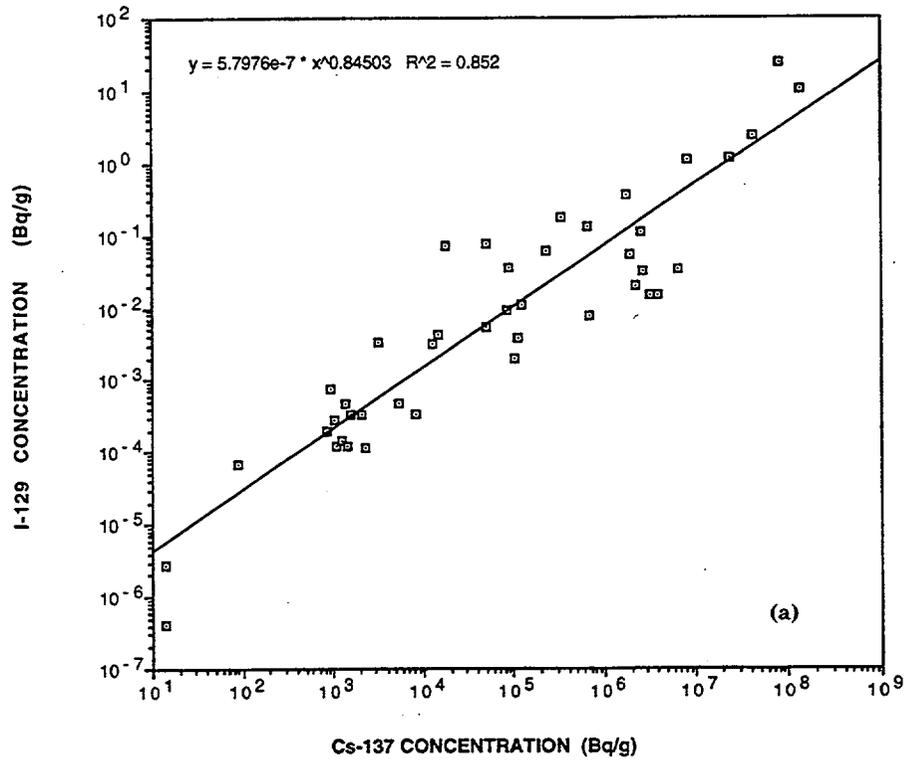
Figures 7.3a, 7.3b   Correlation of I-129 with Cs-137 (a) and I-129 with Co-60 (b) in Commercial Nuclear Power Station Low-Level Wastes

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following reports: NUREG-4101 (Cline, Noyce, Coe, and Wright 1985), NP-4037 (Best and Miller 1985), NP-5077 (Best and Miller 1987), and TR-100641 (James and Vance, 1992). The industry data bases for ^{129}I and ^{99}Tc largely represent detection limits for the LLW samples analyzed and reported by the service analytical laboratories using radiometric methods of analysis. As mentioned earlier, these "less than" values were entirely acceptable for classification of the radioactive waste, but very conservatively overestimate the actual quantities of these radionuclides being sent to LLW shallow-land burial facilities.

Figures 7.5a and 7.5b show the geometric means for measurements made at PNNL and industry scaling factors for ^{129}I and ^{99}Tc for all PWR and BWR data. The PNNL ^{129}I/^{137}Cs scaling factor for PWR stations of 6.48 x 10^{-8} is 26,000 and 4,800 times lower than the scaling factors reported in NUREG-4101 and NP-5077, respectively. For BWR stations, the PNNL scaling factor of 4.25 x 10^{-7} is 1200 and 200 times lower than those reported in NUREG-4101 and NP-5077. The PNNL scaling factors are in very close agreement with the calculated PWR and BWR fuel source term isotopic ratios of ^{129}I and ^{137}Cs computed by the ORIGEN-2 isotope generation code. Best and Miller (1985) have published ORIGEN-calculated isotopic ratios for the 10 CFR Part 61 radionuclides as a function of fuel burnup, and Bhattacharyya, Janati, and Shearer (1987) have conducted a similiar assessment for ^{129}I and ^{137}Cs. The ^{129}I/^{137}Cs activity ratio varies only slightly with burnup, and after a 500 day irradiation period the isotopic ratios for PWR and BWR stations are 2.8 x 10^{-7} and 2.9 x 10^{-7}, respectively (Best and Miller 1985). The ratios reported by Bhattacharyya, Janati, and Shearer (1987) are essentially identical. In addition, more recent measurements of the ^{129}I/^{137}Cs scaling factor for French reactor LLW have shown values very similiar to those measured in the PNNL study (Leuthrot, Ridoux, and Harrer, 1997). Thus, it appears that the iodine and cesium are being leached from the irradiated fuel at about the same rate into the reactor primary coolant and that major fractionation of the two radionuclides does not occur during their transport throughout the various waste streams at the nuclear power stations. For these reasons, it may be appropriate to consider a generic ^{129}I/^{137}Cs industry scaling factor for commercial

nuclear power stations, particularly PWR stations. James (1997) has recently reviewed the use of scaling factors for ^{99}Tc and ^{129}I, and concluded that useful values based on recent, more accurate measurements can be used for estimating the concentrations of these radionuclides in LLW.

For comparison purposes with the industry data base, a PNNL ^{99}Tc/^{137}Cs scaling factor was computed even though the correlation of these two radionuclides was very poor. For PWR stations the PNNL scaling factor of 1.70 x 10^{-6} is 2000 and 460 times lower than the scaling factors reported in NUREG-4101 and NP-5077, respectively. For BWR stations, the PNNL scaling factor of 1.18 x 10^{-6} is 1300 and 290 times lower than those reported in NUREG-4101 and NP-5077, respectively. The industry data base assessment in NP-5077 also recognized that the correlation between ^{99}Tc and ^{60}Co was much better than the correlation with ^{137}Cs, and this report provided a geometric mean value for the ^{99}Tc/^{60}Co scaling factor for PWR stations of 2.3 x 10^{-4}. This value is still about 180 times higher than the PNNL scaling factor of 1.29 x 10^{-6} for PWR station LLW.

The ORIGEN-calculated ^{99}Tc/^{137}Cs activity ratios for 500-day irradiated fuel at PWR and BWR stations are 1.31 x 10^{-4} and 1.33 x 10^{-4}, respectively (Best and Miller 1985), and these values are about two orders of magnitude higher than the measured PNNL ratios. The most plausible explanation for this discrepancy is that the technetium leach rate from irradiated fuel is much lower than that for cesium. Studies of PWR spent fuel dissolution by simulated groundwater have shown that the initial leach rate of Cs from the spent fuel was much greater than for Tc (Wilson 1990). This study also showed that under the proper conditions leached Tc could be reduced, presumably to the +IV oxidation state, and removed from solution on hydrous iron oxides. If this behavior was occurring in reactor coolant water, it could explain the low ^{99}Tc/^{137}Cs ratios observed in the PNNL data, as well as the much better correlations observed between ^{99}Tc and ^{60}Co in LLW.

Similiar behavior is noted for ^{239,240}Pu relative to ^{137}Cs. The ORIGEN-2 code predicts a ^{239,240}Pu/^{137}Cs ratio of 1.17 x 10^{-2} for PWR fuel irradiated for 500 days, whereas the industry PWR data base for LLW gives a geometric mean value of 4.0 x 10^{-4}. This

$y = 9.9730e-5 * x^{0.66778}$ $R^2 = 0.631$
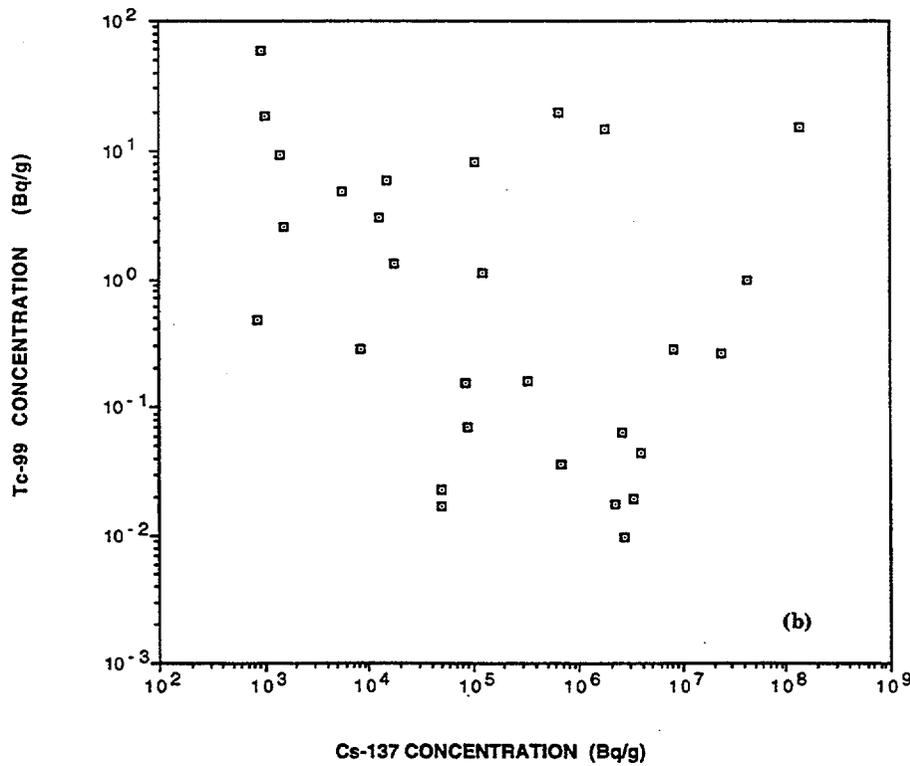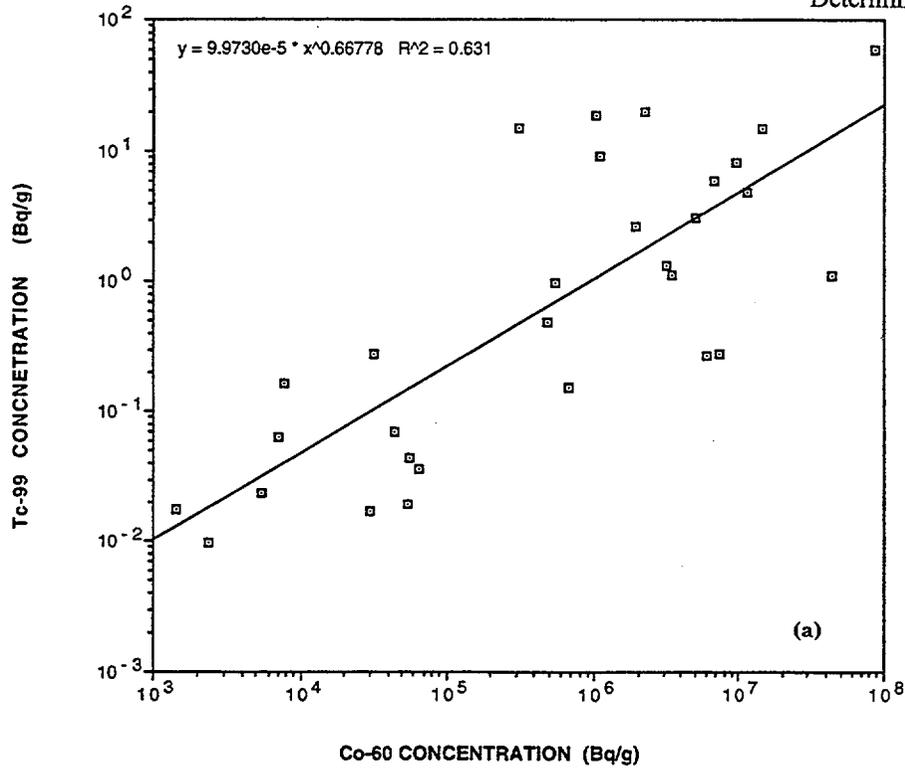
Figures 7.4a, 7.4b   Correlation of Tc-99 with Co-60 (a) and Tc-99 with Cs-137 (b) in
Commercial Nuclear Power Station Low-Level Wastes
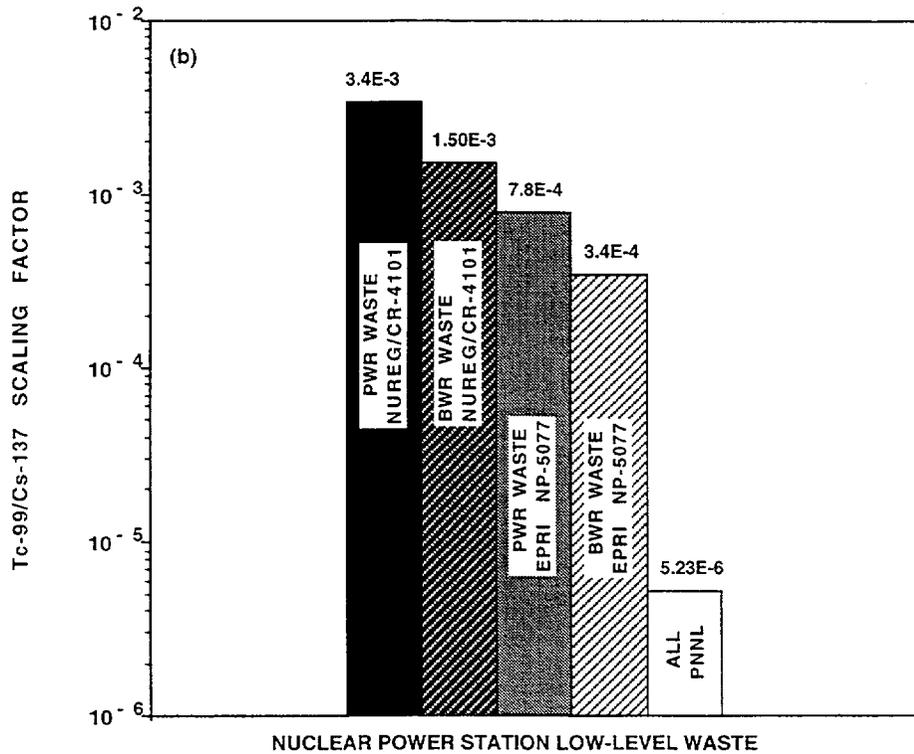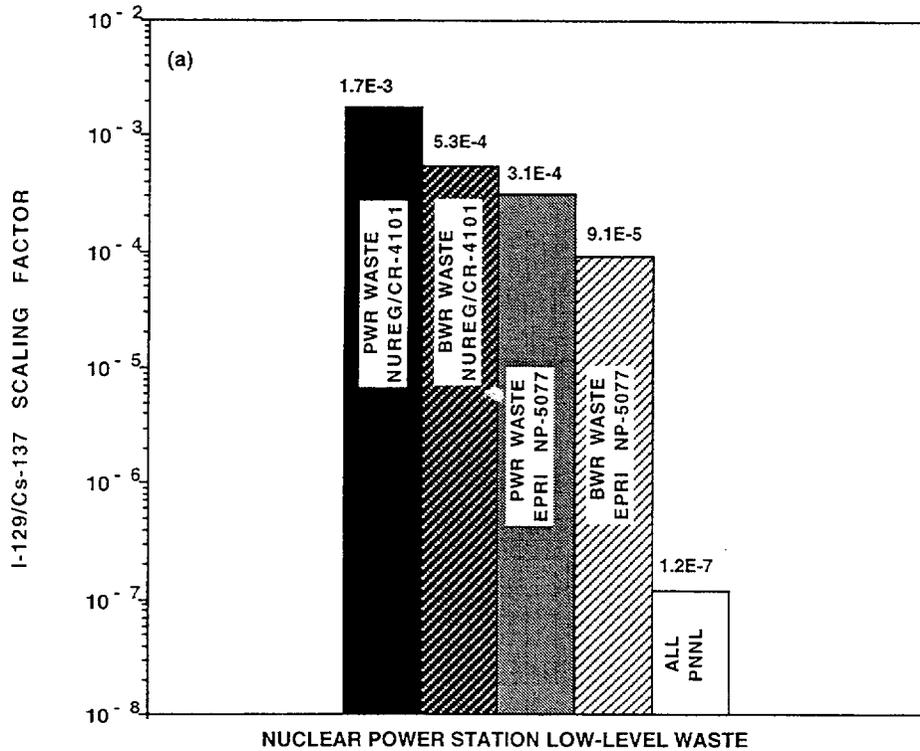
Figures 7.5a, 7.5b   Comparison of Geometric Mean Values for the PNNL and Industry
Activity Scaling Factors for (a) I-129/Cs-137 and (b) Tc-99/Cs-137

difference of a factor of 30 between the predicted fuel source term ^{239,240}Pu/^{137}Cs activity ratio versus the measured ratio in LLW is reasonably similiar to the factor of 77 difference between the predicted fuel source term ^{99}Tc/^{137}Cs ratio versus the measured ratio in LLW. Thus, if a major fraction of the ^{99}Tc in reactor coolant is present as a relatively insoluble reduced species, it would behave similiar to other relatively insoluble radionuclides such as ^{239,240}Pu and ^{60}Co.

7.2.1.6 Conclusions Regarding ^{129}I and ^{99}Tc Scaling Factors

The generic activity scaling factors for ^{129}I and ^{99}Tc developed in this study are believed to be the most accurate data base for these scaling factors, and are the ones recommended for use by the nuclear power industry. Based on the results of the ultra-sensitive mass spectrometric analyses of ^{129}I and ^{99}Tc conducted in this study, the concentrations of these radionuclides and their associated scaling factors in LLW have been shown to be two to four orders of magnitude lower than the corresponding values in the nuclear power industry data bases. This difference is primarily due to the fact that the concentrations of these radionuclides reported in the industry data base are mostly lower limits of detection of the radiometric measurement methods used for their determination by service analytical laboratories.

The quantities of ^{129}I and ^{99}Tc actually deposited in existing LLW disposal facilities has undoubtedly been over-estimated by several orders of magnitude. In addition, site performance assessment modeling of future LLW disposal facilities using the industry data bases to compute the radionuclide inventories at these disposal sites will likewise overestimate the quantities of ^{129}I and ^{99}Tc disposed at a facility by several orders of magnitude. If the true quantities of these two radionuclides were used in the site performance assessment modeling, the ^{129}I and ^{99}Tc would no longer be the limiting radionuclides controlling the total quantity of radioactive material allowed at a LLW disposal facility.

The measured ^{129}I/^{137}Cs scaling factor is in good agreement with the ratio of these radionuclides in the ORIGEN-2 calculated reactor fuel source term.

However, the measured ^{99}Tc/^{137}Cs scaling factor is about 77 times lower than the ORIGEN-2 predicted ratio for the reactor fuel source term. The reason for this difference should be investigated by determining the oxidation state and physicochemical behavior of Tc in the reactor coolant and in LLW. This information is critical to a better understanding of the ultimate fate of ^{99}Tc during the disposal of LLW in shallow-land burial facilities.

It is recommended that the nuclear utilities include a few selected samples of LLW each year to be analyzed for ^{129}I and ^{99}Tc by ultra-sensitive mass spectrometry in their 10 CFR Part 61 compliance radioanalytical program. Although this small number of analyses is far from ideal, the data base that would be generated would be far superior to the overly-conservative scaling factors that are currently being developed and used by the nuclear utilities. An alternative method for estimating more accurate scaling factors would be to utilize one of the computer codes, such as RADSOURCE (Vance, Holderness, James, and Lee 1992) or 3R-STAT (Vance and Associates 1993), for predicting activity scaling factors from reactor coolant isotopic data and other operational parameters. However, it is still recommended that these computer code methods be validated by occasional mass spectrometric analyses of the ^{129}I and ^{99}Tc concentrations in LLW from each station.

7.2.2 Carbon-14 Scaling Factors in LLW and Activated Metal

Similiar problems to those observed for ^{129}I have been documented for ^{14}C values in the industry data base (Vance, Helmholz, and Sutherland 1988). Carbon-14 concentrations are frequently estimated in LLW using ^{14}C/^{60}Co scaling factors, and there are discrepancies in these factors. As shown in Table 7.9, the ^{14}C/^{60}Co scaling factors reported in NUREG/CR-4101 (Cline, et al. 1985) for the BWR and PWR full data bases are 47 and 5.4 times higher, respectively, than the scaling factors reported in EPRI NP-5077 (Best and Miller 1987). In addition, the scaling factors reported in EPRI NP-5077 systematically decreased by two orders of magnitude with increasing sample activity. This is probably a reflection of reporting lower-limit-of-detection (LLD) values or values very near the detection limit

Table 7.9 $^{14}C/^{60}Co$ Radwaste Scaling Factors (from Vance, et al., 1988)

Reference	Sample Type	$^{14}C/^{60}Co$ Scaling Factor	
		BWR	PWR
NUREG/CR-4101[a]	Full Data Base	3.5E-2	6.5E-2
NP-5077[b]	Full Data Base	7.4E-4	1.2E-2
	Low Activity	3.8E-3	5.4E-2
	Medium Activity	7.6E-4	3.6E-3
	High Activity	3.1E-5	9.9E-4

(a)   Cline, Noyce, Coe and Wright, 1985
(b)   Best and Miller, 1987

for ^{14}C in the low and medium activity samples that are one to two orders of magnitude higher than the actual ^{14}C concentrations in the samples. The service analytical laboratories who perform the 10 CFR Part 61 radionuclide analyses generally use very small samples of LLW materials for analysis of ^{14}C because a total destruction of the sample by combustion or oxidative acid dissolution is used, and excessively large quantities of liberated CO_2 would be generated if large amounts of organic matter were present in the samples. Thus, many of the ^{14}C measurements, especially for the low- and medium-activity samples, are made very near the detection limit of the analytical method, and any small variations in instrument background, noise, or statistical fluctuations could result in a false positive signal construed to be due to ^{14}C. Also, the final measurement of the separated ^{14}C is usually done by nonspecific liquid scintillation counting, and any cross-contamination with other more abundant radionuclides in the LLW materials would are result in false positive values for ^{14}C. Thus, the correlation between ^{14}C and ^{60}Co is rather poor, but this is not surprising since the two radionuclides are produced by entirely different mechanisms. Most of the ^{14}C is produced in the reactor coolant by neutron activation (n, alpha) of the ^{17}O present in the water molecules of the reactor coolant. The ^{60}Co is produced by neutron activation of cobalt impurities in metal components used in the reactor pressure vessel (and internals) and in primary loop construction materials.

Very few ^{14}C measurements have been made in neutron-activated metal wastes. Three different types of spent fuel assembly hardware were analyzed for ^{14}C and other long-lived activation products (Robertson, Thomas, Wynhoff, and Haggard 1993). This work, which examined stainless steel, Inconel, and Zircaloy alloys, provided $^{14}C/^{60}Co$ activity scaling factors that varied from 3.67E-5 to 5.49E-3, with a geometric mean of 5.39E-4 for the full data set. This geometric mean is in reasonably good agreement with the industry data bases for high activity wastes from PWR and BWR stations. The concentrations of ^{14}C were dependent upon the concentration of the parent element (nitrogen) in the alloy and the distance from the center of the fueled region of the assemblies to the location of the samples. The ^{14}C in neutron-activated metal components is produced primarily by the reaction

$^{14}N(n,p)^{14}C$ with the nitrogen being present in the metals as the nitride or as interstitial nitrogen gas (Davis 1979). The nitrogen contents of the metal alloys of construction are often not well known, and when specifications are given the nitrogen contents have a considerable range. For this reason, it is difficult to conduct accurate neutron activation modeling estimates of ^{14}C concentrations in irradiated metals, and empirical measurements have provided the most accurate activity scaling factor data.

7.3 Review of Activity Ratios of ^{63}Ni and ^{59}Ni in Low-Level Waste

The nickel radionuclides, ^{63}Ni and ^{59}Ni, are co-produced by neutron activation of the stable nickel isotopes, ^{62}Ni and ^{58}Ni, respectively. The major source materials for the production of these radionuclides are stainless steel and Inconel metals used in reactor construction (see Table 2.3). Because the ^{63}Ni and ^{59}Ni emit very low energy radiations during their decay, they are quite difficult to measure and require very clean radiochemical separations prior to specialized counting methods. In addition, adequate calibration standards of ^{59}Ni have not been commercially available for calibrating counting equipment. Because of these problems, there have been substantial differences in the relative amounts of these two radionuclides reported by various analytical service laboratories.

When 10 CFR Part 61 was first enacted, a large number of analyses of these radionuclides were conducted by service analytical laboratories for a wide variety of LLW samples (Cline, et al., 1980; Cline et al., 1985). These initial measurements provided mean $^{59}Ni/^{63}Ni$ activity ratios of 0.0744 for all BWR waste samples and 0.0355 for all PWR waste samples analyzed. Calculated values of this ratio indicated that the ratio should be much lower, ranging from 0.0075 to 0.0116 depending on the total neutron fluence during irradiation of the neutron-activated material (Evans, et al., 1984; Vance, Helmholz and Sutherland, 1988). Niese and Boden (1995) calculated that the $^{59}Ni/^{63}Ni$ activity ratios in neutron irradiated materials would vary between 0.0054 to 0.0080, depending on the neutron flux and

the irradiation interval. Table 7.10 shows the results of two sets of these calculations. Further assessments showed major discrepancies between calculated and measured values of the ^{59}Ni/^{63}Ni activity ratios in LLW materials (Bedore, Levin and Tuite, 1987; Luksic, 1989; Robertson, et al., 1991).

It now appears that the early measurements of ^{63}Ni and ^{59}Ni in LLW reported by Cline et al (1980; 1985) had significantly higher ^{59}Ni/^{63}Ni activity ratios (perhaps by as much as a factor of 10) compared to more recent values. An examination of individual LLW sample analyses suggests that both systematic and random analytical errors resulted in large uncertainties in the measurement of ^{63}Ni and ^{59}Ni. It also appears that some of the calculated ratios made in other investigations (Luksic, 1989; Robertson, et al., 1991) were in error due to insufficient neutron absorption cross-section data as a function of neutron energy.

The bounding calculations of ^{59}Ni/^{63}Ni activity ratios shown in Table 7.10 should cover the true range of values for these radionuclides in LLW from nuclear power stations, and ratios ranging from 0.005 to 0.012 would be possible. In any case, the ^{63}Ni, rather than the ^{59}Ni, would always be the nickel radionuclide that would control the waste classification criteria specified in 10 CFR Part 61.

Table 7.10   Comparison of Calculated ^{59}Ni/^{63}Ni Activity Ratios in Neutron-Irradiated LLW Material

Vance, Helmholz and Sutherland (1988)

Thermal Neutron Flux (n/cm²/s)	Irradiation Period (years)	Activity Ratio (Ni-59/Ni-63)
1.3E11	1	0.0076
	3	0.0077
	10	0.0079
	30	0.0084
1.3E13	1	0.0116
	3	0.0114
	10	0.0108
	30	0.0094

Niese and Bolen (1995)

Thermal Neutron Flux (n/cm²/s)	Irradiation Period (years)	Activity Ratio (Ni-59/Ni-63)
1.0E12	1	0.0079
	2	0.0080
	5	0.0080
1.0E13	1	0.0079
	2	0.0078
	5	0.0077
1.0E14	1	0.0072
	2	0.0067
	5	0.0054

8 Summary, Conclusions, and Recommendations

This project has examined the occurrence and some of the potential radiological and environmental impacts of a number of very long-lived radionuclides produced in LLW generated at commercial nuclear power stations. The study has focused on a group of additional radionuclides that are not specified in 10CFR61, but that are produced in neutron activated metal components of reactor internal hardware and in primary coolant demineralization resins that make up a significant part of the LLW streams from commercial nuclear power stations. These radionuclides include ^{10}Be, ^{36}Cl, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, and ^{121m}Sn. In addition to this group of radionuclides, the specified 10 CFR Part 61 radionuclides were also measured in the selected samples.

Of the group of additional radionuclides measured in this project, ^{10}Be, ^{36}Cl, and ^{108m}Ag appear to have the greatest potential impact with respect to 10 CFR Part 61. Although none of these radionuclides are present in LLW in quantities high enough to seriously impact the current LLW classification and shallow-land disposal criteria specified in 10 CFR Part 61, further radiological and environmental assessments should be considered to determine if they should be amended to 10 CFR Part 61. It is recommended that further studies be focused on: 1) providing an accurate assessment of the total quantities of these radionuclides in LLW from these sources, 2) determine the leaching characteristics of these LLW materials, 3) determine the migration behavior and environmental pathways of these radionuclides upon release from LLW disposal facilities, and 4) provide performance assessment modelers with the necessary radiological/geochemical information to better predict the potential impacts from disposal of this group of radionuclides.

Beryllium-10 is of special interest because of its potential to be produced in relatively large quantities in nuclear power station LLW, originating in spent BWR and PWR control rods and in spent primary coolant demineralization resins. The ^{10}Be is produced by neutron activation of ^{10}B present as neutron absorbing materials, boron carbide and borosilicate glass in control rods, and as soluble borate added to PWR reactor coolant. The extremely long half-life of ^{10}Be (1.6E6 years), together with a relatively high ingestion dose conversion factor and a

relatively low Kd value for adsorption onto sandy types of soil, create the potential for long-term migration and offsite radiation exposure of this radionuclide from LLW disposal facilities. This study has shown that ^{10}Be could be the third most abundant radionuclide in spent control rods and in some PWR spent primary resins after a decay time of about 600 years. Therefore, it is recommended that further studies be conducted to: 1) provide an accurate assessment of the total quantities of ^{10}Be contained in LLW from these sources, 2) determine the ^{10}Be leaching characteristics from LLW, 3) determine the migration behavior and environmental pathways of ^{10}Be released from LLW disposal facilities, and 4) provide performance assessment modelers with the necessary radiological/geochemical information to evaluate the potential impacts from disposal of this radionuclide in LLW.

Silver-108m is also of interest because of its production in large quantities in PWR spent RCCA control rods which contain 80% silver. Silver-108m has a 130 year half-life and a relatively high ingestion dose conversion factor due to its multiple high-energy gamma-ray emissions. Silver-108m will easily be the most abundant radionuclide in spent RCCA control rods for many hundreds of years. It is therefore of some concern from a waste disposal perspective. Fortunately, the stable metallic waste form and the expected high soil Kd values should minimize the leaching rate and offsite transport of this radionuclide during water infiltration at a LLW disposal facility. Nevertheless, it is recommended that further studies be conducted for ^{108m}Ag, as described in the above paragraph for ^{10}Be, to better understand the radiological, environmental, and health impacts associated with the disposal of neutron-activated metal components containing ^{108m}Ag.

Chlorine-36 is the other very long-lived radionuclide measured in this study that deserves further assessment from a LLW disposal standpoint. Its very long half-life (3.01E5 years), relatively high ingestion dose conversion factor, and high environmental mobility combine to create the potential for long-term migration from a LLW disposal facility. Fortunately, the concentrations of

^{36}Cl in LLW from commercial nuclear power stations are quite low. Chlorine-36 is produced almost exclusively in nuclear power plants by neutron activation of soluble chloride impurities present in the reactor coolant water, and is then concentrated on primary demineralization resins. Because chloride ions accelerate the corrosion of stainless steel in the reactor primary loop, great care is taken to minimize the chloride concentrations in reactor coolant water, and typical concentrations are in the low ppb range. This is sufficient to produce about 0.0001 to 0.002 uCi/g of ^{36}Cl in spent primary resins. This equates to an estimated 0.2 to 5 Ci/y of ^{36}Cl in primary resin LLW from all PWR nuclear power stations in the U. S. As discussed in Section 6.1 of this report, LLW disposal site performance assessment modeling, using a source term containing only 0.1 Ci of ^{36}Cl was sufficient to predict that this radionuclide would be the major contributor to the offsite radiation dose for the contaminated well/drinking water exposure scenario. Because of this potential for radiation exposure, it is recommended that further studies similar to those described in the above paragraph for ^{10}Be be conducted to obtain a better understanding of the radiological and environmental impacts from disposal of this radionuclide in LLW.

The other additional radionuclides measured in this study, ^{93}Mo, ^{113m}Cd, and ^{121m}Sn, either have half-lives that are too short to be of consequence in LLW disposal, or in the case of ^{93}Mo, the concentrations do not appear to be high enough to contribute significantly to the potential radiation exposure.

Activity scaling factors have been developed for all of the additional radionuclides measured in this study. The use of activity scaling factors for estimating the concentration of a radionuclide in LLW is permitted by 10 CFR Part 61.55, and this method is desirable for radionuclides such as those listed above that are difficult to measure directly in LLW materials. Consistent scaling factors for a wide variety of LLW materials were determined for ^{93}Mo and ^{93m}Nb relative to ^{60}Co over a concentration range of four orders of magnitude. Generic scaling factors for the other long-lived radionuclides measured in this study showed much greater variability due to the unique composition of some of the materials. However, in some cases useful scaling factors were obtained when similiar LLW materials were

considered as a group. Because of the potential for offsite migration of ^{36}Cl from a LLW disposal facility, it is recommended that more analyses of spent ion exchange cleanup resins (the major source of ^{36}Cl in LLW from nuclear power stations) to develop a better data base of activity scaling factors.

Recent measurements and assessments of ^{129}I and ^{99}Tc in LLW from commercial nuclear power stations have shown that the true concentrations of these radionuclides are several orders of magnitude lower than previously reported values. Very sensitive mass spectrometric analytical methods were utilized to determine the concentrations and activity scaling factors for ^{129}I and ^{99}Tc in a wide variety of LLW samples from a number of PWR and BWR stations in the U. S. (Robertson, et al., 1997). These measurements provided concentrations and associated activity scaling factors (relative to ^{137}Cs and ^{60}Co) for these radionuclides that were two to four orders of magnitude lower than the very conservative values published in several nuclear power industry data bases. Geometric mean values of the ^{129}I/^{137}Cs scaling factor for LLW from PWR and BWR stations measured in this study were 6.48 x 10^{-8} and 4.25 x 10^{-7}, respectively. The geometric means for ^{99}Tc/^{137}Cs in LLW from PWR and BWR stations were 7.37 x 10^{-7} and 3.21 x 10^{-4}, respectively. The correlations between ^{99}Tc and ^{60}Co were considerably better than the correlations between ^{99}Tc and ^{137}Cs, and the geometric mean values of the ^{99}Tc/^{60}Co ratios for PWR and BWR stations were 1.70 x 10^{-6} and 1.18 x 10^{-6}, respectively. Due to the dual production modes for ^{99}Tc (neutron activation of molybdenum and fission of ^{235}U), it is recommended that a closer examination of the ^{99}Tc activity scaling factors be conducted to develop more accurate scaling factors for the specific modes of production at reactor stations that are dominated by one or the other production modes.

Because performance assessment modeling studies of LLW disposal facilities have indicated that ^{129}I and ^{99}Tc (as well as ^{14}C) will be the limiting radionuclides with regard to the total quantities of LLW permitted at a site, it is important to determine as accurately as possible the actual quantities of these radionuclides being disposed in LLW. The mass spectrometric measurements performed during this study have clearly shown that when the true concentrations and

activity scaling factors are used for performance assessment modeling, the ^{129}I and ^{99}Tc no longer become limiting radionuclides for LLW inventories at disposal facilities. Disposal facilities will, therefore, be able to accommodate larger quantities of LLW at each facility, thereby minimizing the expense of developing additional disposal sites.

An assessment of the ^{63}Ni and ^{59}Ni production and activity scaling factors in LLW indicates that early reported values of the ^{59}Ni/^{63}Ni activity ratio were too high by up to factors of 5 to 10. More recent analyses and assessments indicate that this ratio should range between about 0.006 to 0.012, depending upon the neutron flux and the irradiation time of the exposed materials. In any event, this activity scaling factor does not appear to be a critical parameter with respect to 10 CFR Part 61 waste classification criteria because the ^{63}Ni, rather than ^{59}Ni, will always be the controlling radionuclide of the two nickel radionuclides in LLW classification.

Because all of the above radionuclides measured in this study do not have energetic gamma radiations and are very difficult to measure, it is desirable to apply activity scaling factors (developed from the empirical measurements) for estimating their concentrations in LLW materials. Table 8.1 presents a summary of the scaling factors developed during this study and from previous analyses of LLW materials conducted at PNNL. The ^{93}Mo/^{60}Co, ^{93m}Nb/^{60}Co, ^{99}Tc/^{60}Co, and ^{129}I/^{137}Cs activity scaling factors are quite consistent over a wide range of LLW materials and concentrations, and generic scaling factors can be applied for these radionuclides. These radionuclides have been very carefully measured by either ultra-sensitive mass spectrometric methods or by state-of-the-art radiochemical separations and counting techniques. They are, therefore, considered to be the most accurate activity scaling factors in existence for these radionuclides. For the other radionuclides measured in this study, useful scaling factors can be developed for specific types of LLW materials, and these scaling factors are shown in Table 8.1. A number of these specific scaling factors have been developed using "less-than" concentration values for samples where the actual concentrations were below the analytical limit of detection. These specific scaling factors should be useful for estimating concentrations, or lower-limits-of-detection, of these radionuclides in various types of LLW materials as shown in Table 8.1.

Table 8.1 Summary of Measured Activity Scaling Factors for Additonal Radionuclides

Radionuclide	Scaling Radionuclides	Sample Type	Number of Samples	Activity Scaling Factor Geometric Mean
^{93}Mo	^{93}Mo/^{60}Co	All (Table 7.1)	22	1.6E-6*
^{93m}Nb	^{93m}Nb/^{60}Co	All (Table 7.2)	22	6.9E-4
^{10}Be	^{10}Be/^{60}Co	Control Rods[A] Spent Resin[B] Metals[C]	3 3 5	2.4E-3 2.1E-4* 9.0E-6*
^{36}Cl	^{36}Cl/^{60}Co	Spent Resin[B] Metals[C]	3 4	6.0E-5 2.4E-5*
^{113m}Cd	^{113}Cd/^{60}Co	Spent Resin[B] Metals[C] Cd Alloy[D]	2 3 4	8.8E-4 3.1E-4 0.65
^{108m}Ag	^{108m}Ag/^{60}Co	Spent Resin[B] Metals[C] Ag Alloy[E]	2 4 6	6.6E-4* 2.6E-3* 9.1
^{121m}Sn	^{121m}Sn/^{60}Co	Spent Resin[B] Metals[C]	2 3	4.5E-5* 1.5E-4*
^{129}I	^{129}I/^{137}Cs	All (Table 7.8)	45	1.20E-7
^{99}Tc	^{99}Tc/^{137}Cs ^{99}Tc/^{60}Co	All (Table 7.8) All (Table 7.8)	31 31	5.23E-6 1.67E-6

* Scaling factor comprized of two or more "less-than" values.

A.   Control rod materials containing ^{10}B$_4$C and ^{10}B enriched glass.

B.   Spent reactor coolant cleanup resin and liquid radwaste cleanup resin.

C.   Stainless steel and inconel hardware from control rod assemblies.

D.   5% Cd alloy used in RCCA control rod assemblies.

E.   80% Ag alloy used in RCCA control rod assemblies.

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Appendix A

Radiochemical Procedures for Additional Long-Lived Radionuclides

A.1 Pre-Treatment of Ion Exchange Resin, Neutron-Activated Metal, and solid LLW Samples Prior to 10CFR Part 61 Radionuclide Analyses

Ion Exchange Resins and Dry Active Waste

Sample aliquots of spent ion exchange resin and solid dry active waste (DAW) were leached in acid to solubilize the radionuclides of interest in preparation for 10CFR Part 61 radiochemical analyses. Sample sizes ranging from 0.1 to 50 grams, depending upon the activity of the material, were contacted with hot (100°C)6N HCl for 20 minutes. This leaching was repeated twice more. The combined acid leachate was cooled and brought to a standard volume with 6N HCl. This served as the stock solution for further aliquoting and radiochemical analyses.

Neutron-Activated Metal Specimens

Because of the very high activities and gamma dose rates, most samples of neutron-activated metal were cut into small pieces inside of the PNNL hot cell facilities. To eliminate any fission product and TRU contamination of the metal specimens which could have occurred during operations in the hot cell, the metal samples were repeatedly (3-5 times) leached with hot acid in a clean fume hood to remove any hot cell contamination prior to dissolving the metal specimens for analyses. The stainless steel specimens were pre-cleaned by leaching with hot 6N HCl. Inconel and zircaloy samples were leached with hot 6N HCl followed by hot 6N HNO_3 containing one mL of HF. The Ag-Cd-In alloy was leached with hot 6N HNO_3. The cleaned metal specimens were then dissolved in hot 6N acid of the same types used for the leaching. The solutions of acid-dissolved metal were then cooled and brought to a standard volume with the appropriate acids. These acid solutions served as the stock solutions for further sample aliquoting for radionuclide analyses.

A.2 Detailed Radiochemical Procedures

Beryllium-10 Procedures

1. To an aliquot of resin acid leach or metal acid dissolution, add 20 mg Be carrier and ^{7}Be tracer.

2. Add 5 mg each of Co, Ni, Sr, and Cs carriers and make basic with NH_4OH. Let sample stand for 1 hour. Centrifuge, discard supernate, wash precipitate (ppt) with water, discarding wash.

3. Dissolve ppt in a few mL of 1N HCl and repeat step 2.

4. Repeat step 3.

5. Dissolve ppt in 1M HCl, add 10 mg Eu carrier and 1 mL of saturated oxalic acid. Adjust solution to pH 3-4 with NH_4OH. Heat and filter, discarding ppt.

6. Adjust solution to 10M HCl and pass through an anion resin column, Cl⁻ form, 100-200 mesh, that has been equilibrated with 10M HCl. Save effluent and wash column with 5 mL 10 M HCl, adding wash to effluent. Evaporate to about 5 mL.

7. Make solution pH 10 with NH_4OH. Centrifuge and discard supernate. Wash ppt twice with water, discarding washes. Determine yield by measuring the volume of $Be(OH)_2$ ppt and comparing to volume of 20 mg Be carrier precipitated as $Be(OH)_2$. Dissolve ppt with 5 mL of 0.1M HCl and transfer solution into a scintillation vial, add Ultima Gold® scintillator and beta count in the Quantilus® liquid scintillation.

Chlorine-36 Procedure

1. To sample aliquot of the HCl acid dissolution or leach which contains up to 100 mg of Cl ion per mL of solution, adjust sample acidity to 1M with water and add ^{38}Cl tracer.

2. Prepare a cation resin column, $^+$H form, 100-200 mesh (1cm x 15cm). Pass sample aliquot through column, saving effluent. Wash column with 5ml of 0.01M Chl. Combine wash and effluent. Discard resin.

3. To solution, add stoichiometric amount of silver nitrate solution, stir, centrifuge, check for complete precipitation of AgCl and discard supernate. Wash ppt twice with 10 mL of 2M HNO_3. Discard washes. Wash ppt twice with water, discarding washes.

4. Slurry ppt with 5 mL of water and transfer to a scintillation vial. Gamma count for yield. Suspend ppt in Insta-Gel® and count in Quantilus® liquid scintillation spectrometer to determine ^{36}Cl.

Iron-55 Procedure

1. To sample aliquot in a 50 mL beaker, add enough Fe carrier to give 5 mg. Add 10 mg each Cs, Ni, Co, Sr. Make basic (pH 10-12) with fresh NH_4OH. Stir for about 5 minutes. Let stand for 1 hr.

2. Transfer to centrifuge cone, centrifuge and discard supernate.

3. Dissolve ppt in several mL of dilute HNO_3, add 10 mg each Cs, Ni, Co, Sr carriers. Make basic (pH 10-12) with fresh HN_4OH. Stir for about 5 minutes. Let stand for 1 hr.

4. Transfer to centrifuge cone, centrifuge, discard supernate.

5. Dissolve ppt in 20 ml of 4M HCl, add 10 grams of anion resin that has been equilibrated in 4M HCl. Stir for 15 minutes, filter, wash with 10 ml of 4M HCl. Discard filtrate and wash.

6. Elute Fe by passing three 10 mL portions of 0.01M HCl through the resin filter bed. Save eluate and discard resin.

7. Evaporate eluant, transfer to a tared planchet,

and gravimetrically determine yield. Dissolve Fe with 5 mL 0.1M HCl, transfer to scintillation vial and add Ultima Gold® and count in Quantilus® liquid scintillation spectrometer for ^{55}Fe.

Nickel-59,63 Procedure

1. To an aliquot of resin acid leach or acid dissolution of metal, add 20 mg each of Ni, Co, and Fe carriers. Evaporate to just dryness.

2. Dissolve in small amount of 1M HCl, transfer to centrifuge cone and make basic with NH_4OH (pH 9). Centrifuge and discard ppt. To supernate, add 1 mL of 1M ammonium tartrate and 1 mL 6M NH_4Cl. Add 5 mL of saturated dimethyl glyoxime (DMG), stir, and let stand for 30 minutes.

3. Centrifuge, discard supernate, dissolve ppt with 8 M HNO_3, transfer to small beaker, and evaporate to near dryness. Add 5 mL conc. HCl and evaporate to near dryness. Add 5 mL conc. HCl, 1 drop of 4M H_2SO_4, and evaporate to near dryness.

4. Add 5 mL 1M HCl, 1 mL 1M ammonium tartrate, 1 mL 6M NH_4Cl, and make basic with NH_4OH to pH 9. Add 5 mL of saturate DMG, stir, and let stand for 30 minutes.

5. Centrifuge, discard supernate, dissolve ppt with 8M HNO_3, transfer to a small beaker and evaporate to near dryness. Add 5 mL conc. HCl and heat to near boiling, add 0.1 mL of 4M H_2SO_4, and heat to near dryness. Add conc. HCl and evaporate to dryness.

6. Dissolve reside in 10 mL of water, divide sample in two equal parts, placing one portion in a scintillation vial and the other in a clean beaker.

7. To the portion in the scintillation vial, add Ultima Gold® and beta count in a Quantulus® liquid scintillation counter for ^{63}Ni.

8. To portion in the beaker, add 1 mL of H_2SO_4,

thymol blue and add NH_4OH until color is gold-green. Electroplate for 1-2 hours on a tared stainless steel disc. Wash disc with alcohol, dry and place in drying oven at 100°C for 30 minutes. Weigh, cover with Mylar®, and count on Low Energy Photon Spectrometer (LEPS) for 100 minutes for ^{59}Ni. Calculate yield gravimetrically.

Strontium-90 Procedure

1. Place an appropriate aliquot of sample in a 50 mL beaker. Prepare reagent blanks and a 10 mL standard of ^{85}Sr.

2. Add 5 mg each of Co and Cs carriers and about 150 dpm ^{85}Sr tracer to each sample. Evaporate the samples to dryness on a hot plate. Dissolve the residue in 5 mL 8M HNO_3.

3. Prepare a Sr-Spec® column for each sample by removing the bottom plug and cap, press the top frit down to the resin surface and let the water drain out. Add 5 mL 8M HNO_3 and let the solution drain through the column.

4. Transfer the sample solution to the reservoir of the column.

5. Rinse the beaker three times with 3 mL portions of 8M HNO_3 (let one solution pass completely through the column before adding the next and rinse the column reservoir well with each addition). Wash the column with an additional 40 mL 8M HNO_3. Discard the washes.

6. Cap the column on both ends and heat-seal in plastic. Perform a quick gamma count to determine whether or not any ^{60}Co or ^{137}Cs remain on the column. If no ^{60}Co or ^{137}Cs are present, return the column to the column stand, remove the cap and plug, and wash the column with 5 mL of 8M HNO_3. Record the time of the last wash. If there is ^{60}Co or ^{137}Cs remaining on the column, wash the column with additional 8M HNO_3, recording the time of the last wash.

7. Elute the Sr with 10 mL H_2O into a liquid scintillation vial. Count this fraction on a gamma detector to determine the ^{85}Sr yield.

Compare with the 10 mL ^{85}Sr standard prepared at the beginning of the procedure to determine yield.

8. After the gamma count, evaporate the samples to dryness in the liquid scintillation vial under a

Niobium-93m, 94 Procedure

1. To an aliquot of sample, add 5 mg of each of the following carriers, Ni, Sr, Fe, Co, 20 mg Sb carrier and 50 mg Nb carrier. Also, add a ^{95}Nb tracer to each sample.

2. Make the samples just basic (pH 8) with carbonate-free NaOH. Centrifuge the sample. Discard the supernate.

3. Dissolve the precipitate resulting from step two in 2M HNO_3. Make the sample basic with NH_4OH. Centrifuge. Discard the supernate.

4. Dissolve the precipitate from step 3 with 5 mL conc. HF. Add 5 mg Co carrier and 20 mg Sb carrier to the sample. Mix the sample well. Transfer the sample to a beaker containing 150 mL conc. HNO_3.

5. Heat the solution on a hot plate using a Teflon covered stir bar. Continue heating and stirring until the sample volume is reduced to at least half of the original volume. Cool the solution and transfer to a centrifuge tube with conc. HNO_3. Centrifuge and discard the supernate.

6. Rinse the ppt three times with water, centrifuging and discarding the wash each time.

7. Dissolve the ppt in 5 mL conc. HF, repeating steps 4, 5 and 6. A very fine white precipitate will be evident.

8. Transfer the washed ppt to a 2-inch diameter planchet. Dry under a heat lamp and cover with two layers of Mylar®.

9. Count the ^{93m}Nb on the Low Energy Photon Spectrometer (LEPS0). Following the LEPS count, count each sample on a gamma detector for a 1000 minute count of the ^{94}Nb, and ^{95}Nb

tracer for yield determination.

Technetium-99 and Molybdenum-93 Procedure

1. To sample aliquot add 1 mg Re carrier, ^{99}Mo tracer/carrier, adjust to 1M HCl, add 1 drop of a 5% NaOCl solution, and pass through a prepared cation resin ($^{+}$H, 100-200 mesh) column. Save effluent, wash column with 5 mL of 0.01 M HCl, adding wash to effluent and discarding resin.

2. Pass supernate through a TEVA-Spec® column. Discard effluent. The Mo and Tc both stay on the column. Wash column with pH 8 NH$_4$OH, discarding wash.

3. Remove top frit from column, extrude resin from the column into a preweighed plastic cup and dry at 100°C for 1 hour. Reweigh, cover with Mylar® and count Mylar® side toward LEPS detector for yield determination.

4. Allow 67-hour ^{99}Mo tracer to decay away, then recount on the LEPS detector for the 16-kev x-rays of ^{93}Mo. Correct ^{93}Mo for both yield and self-absorption due to the TEVA-Spec material.

5. Slurry resin with 5 mL of water and transfer to a scintillation vial. Add Insta Gel® scintillation cocktail, shake, and count in the Quantilus® liquid scintillation spectrometer for ^{99}Tc determination.

Cadmium-109, 113m Procedure

1. To aliquot of resin acid leach or the acid dissolution of the metal, add ^{115}Cd tracer. Add 5 mg Co and 20 mg Ag carriers.

2. Dilute sample to 15 mL with 0.1M HNO$_3$. Add sufficient HCl to ppt the silver present. Heat to coagulate ppt, filter and discard filter.

3. To filtrate, add 20 mg of Ag carrier. If necessary, add additional HCl to ppt the AgCl. Heat, let stand and filter, discarding filter.

4. Add Fe carrier, co-precipitate Cd on Fe(OH)$_3$, making first basic with NaOH. Centrifuge, discarding supernate. Dissolve ppt with 1M HCl.

5. Pass solution through an anion resin column previously equilibrated with 1M HCl. Wash column with 1M HCl, discarding both effluent and wash.

6. Elute Cd with 7.5M NH$_4$OH. Evaporate to dryness to eliminate NH$_3$ salts.

7. Dissolve residue to 0.1M HCl, make pH 8 with NaOH, add 10 mL 1M thioacetamide and heat to form CDS ppt.

8. Centrifuge, transfer ppt to a scintillation vial and gamma count for yield and ^{109}Cd determination.

9. Transfer CDs ppt to a beaker with conc. HNO$_3$. Evaporate to dryness, ad conc. HNO$_3$ and evaporate to dryness. Add 6M HCl to beaker and evaporate to dryness.

10. Dissolve CdCl$_2$ residue with 5 mL of 0.1M HCl and transfer to a scintillation vial. After ^{115}Cd has decayed, add Ultima Gold® scintillator and count in a Quantilus® liquid scintillation beta spectrometer for ^{113m}Cd determination.

Tin-121 Procedure

1. To a sample aliquot, add 20 mg each of Sn(II), Co, Ni, Nb and Cs carriers. Add ^{117m}Sn tracer and 2-3 mL of HCl and evaporate to just dryness.

2. Add 4.5 mL H$_2$SO$_4$ and a few drops of H$_2$O$_2$ and heat to fumes. Allow the sample to cool.

3. Dissolve the sample in 12 mL water and chill in an ice bath for at least a half hour. Add 4.0 mL 5M KI to each sample and mix well. Pour the sample into a separatory funnel, along with 20 mL toluene, and shake vigorously for several minutes. Allow the phases to separate and drain off the aqueous phase into a beaker. Drain the toluene into another clean beaker and then pour

the aqueous fraction back into the separatory funnel. Add 20 mL of fresh toluene to the separatory funnel and shake well.

4. Allow the phases to separate and drain the aqueous phase from the separatory funnel. Return the first toluene fraction to the separatory

funnel containing the toluene from the second extraction.

5. Wash the toluene fractions twice with 15 mL of 3.6M H_2SO_4 - 1M KI. Discard thee washes.

6. Back extract the Sn from the toluene by placing 10 mL of 0.9M H_2SO into the separatory funnel and shaking vigorously for several minutes. Allow time for the two phases to separate.

7. Drain the aqueous phase into a 50-mL centrifuge tube. Make the solution pH 8 with NaOH. Add 10 mL of thioacetamide, stirring well. Heat the tubes in a hot water bath and cool. Centrifuge the samples discarding the supernate.

8. Transfer the ppt to a beaker with 5-6 mL conc. HNO_3. Heat to destroy the sulfide and to form SnO_2. Dilute the precipitate with 15 mL of hot water. Cool and centrifuge the sample, discarding the supernate.

9. Slurry the precipitate with 5.0 mL of water and transfer to a liquid scintillation vial. Prepare the samples appropriately for gamma counting and count the ^{117m}Sn to determine the yield.

10. Suspend the slurried precipitate in Insta-Gel® liquid scintillation cocktail and count in the Quantulus® liquid scintillation spectrometer to determine the amount of ^{121}Sn in the sample.

Pu, Am-Cm and U Procedure

1. To sample aliquot add ^{242}Pu, ^{243}Am, and ^{232}U tracers. Evaporate to dryness.

2. Dissolve residue in 2-3M HNO_3, make 0.1M in ferrous sulfamate and 0.1M in ascorbic acid and stir for 10 minutes.

3. Pass solution through a TRU-Spec® column that has been conditioned by passing through 5 mL of 2-3M HNO_3. Wash column with 10 ml of 2-3M HNO_3 to which 0.1 ml of saturated $NaNO_2$ has been added. Discard wash.

4. Elute Am with 15 mL of 4M HCl.

5. Elute Pu with 15 mL of 4M HCl to which 0.3 mL of a 30% $TiCl_3$ solution has been added.

6. Elute U with 15 mL of a 0.1M ammonium oxalate solution.

Co-ppt Method for Alpha Energy Analysis (AEA)

1. Take 10 mL of 1M HCl and add 100 ug Nd^{3+}, place in a plastic beaker, and add 1 mL of 48% HF, mix and let stand for 30 minutes. Filter through a 25 mm polysulfone filter. Repeat this step to make 3 thin pads of NdF_3 ppt. Save.

2. To eluant from Step 4, evaporate to small volume, and adjust to about 1M HCl. Add 100 ug Nd^{3+} and 1 mL of 48% HF and let stand for 30 minutes. Filter through one of the beds prepared in Step 1. Mount, dry and count on a SiLi alpha energy analyzer.

3. To eluant from Step 5, treat like Step 2 for determination of Pu Isotopes.

4. To eluant from Step 6, treat like Step 2 for determination of U isotopes.

Appendix B

Environmental Considerations of Additional Long-Lived Radionuclides

B.1 Environmental Considerations of Additional Long-Lived Radionuclides

Of the additional long-lived radionuclides examined in low-level waste in this study, only ^{108m}Ag, ^{10}Be, ^{36}Cl, and perhaps ^{113m}Cd appear to be of sufficient concentrations in some types of low-level wastes to be of a potential environmental concern during LLW disposal. The two most important processes affecting environmental mobility are: 1) the leachability of the radionuclides from the wastes by infiltrating groundwater, and 2) the soil retention properties of the radionuclides, i. e., the distribution coefficient, Kd.

The expected leachability of this group of radionuclides is diverse. The ^{108m}Ag and ^{113m}Cd leachabilities are expected to be low because they will be present in activated metal having relatively low corrosivity. The ^{10}Be present in primary coolant demineralization resins will be more readily available for leaching, but the ^{10}Be present in reactor control rods will be in boron carbide and borosilicate glass which should have low leachabilities. The ^{36}Cl present in primary coolant demineralization resins will probably be readily leachable. However, no quantitative information is available to assess the rates and magnitude of the leachability of these radionuclides.

The soil adsorption properties for the additional long-lived radionuclides are listed as ranges of distribution coefficients (Kd) in Table 6.2. For all elements except Cl and Mo, the soil Kd values are relatively high and indicate that soil retention will be sufficiently high to efficiently retard their migration when water infiltration and leaching of the waste occurs. Beryllium-10 could have relatively low Kd values in some types of sandy soils, and together with its very long half-life (1.6 million years), the potential for offsite migration is considerable over very long periods of time.

The ^{36}Cl and the ^{93}Mo will be leached as anions which will migrate readily in groundwater. Chlorine-36 has always been viewed as a conservative radionuclide in the soil/groundwater environment and is, in fact, used for age dating groundwaters because of its minimal retardation characteristics. Because of its high leachability and environmental mobility, even the small quantities of ^{36}Cl expected in LLW could significantly contribute to the offsite radiation dose of the contaminated groundwater ingestion pathway (Campbell, 1994).

The generally low ^{93}Mo concentrations in most activated metal LLW, together with the expected low leachability of the host metals (stainless steel and Inconel) should release relatively small quantities of this radionuclide to the offsite environs.

Table B.2   **Estimated Range of Distribution Coefficient (Kd) Values for Elements Having Long-Lived Radioisotopes**

Element	Range of Distribution Coefficients-Kd (mL/g)
Be	50-700 (sandy topsoil) [a] 800-12,000 (sandy loam topsoil)[a]
Mo	~23 (allurium)[b]
Cl	0-4[a]
Nb	530-5100 (allurium)[b] 180-2900 (bentonite)[b]
Sn	1000-3000 (sandy topsoil)[a] 4400-11,000 (sandy loam topsoil)[a]
Ag	
Cd	1300-16.900[c]

(a)   Serne, et al., 1993
(b)   Erdal, et al., 1977
(c)   Del Debbio, 1989

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11. ABSTRACT *(200 words or less)*

This study focused on identifying and characterizing a group of very long-lived radionuclides that are not specified in 10 CFR Part 61, but which are present in significant concentrations in various types of LLW materials generated at commercial nuclear power stations. The concentrations of ^{10}Be, ^{36}Cl, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, and ^{121m}Sn (as well as the specified 10 CFR Part 61 radionuclides) have been measured in a variety of neutron-activated metal and spent primary demineralization resin LLW samples obtained from U.S. nuclear power stations. Of this group of radionuclides, the ^{10}Be, ^{36}Cl, and ^{108m}Ag appear to be present in some types of LLW materials in sufficient quantities to warrant further investigations to better assess their radiological and environmental impacts associated with LLW disposal. In addition to these radionuclides, an assessment was conducted to provide an updated understanding of the occurrence, distribution, and activity scaling factors of ^{14}C, ^{99}Tc, and ^{129}I, as well as an evaluation of the ^{59}Ni/^{63}Ni activity ratio in LLW.

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silver-108m

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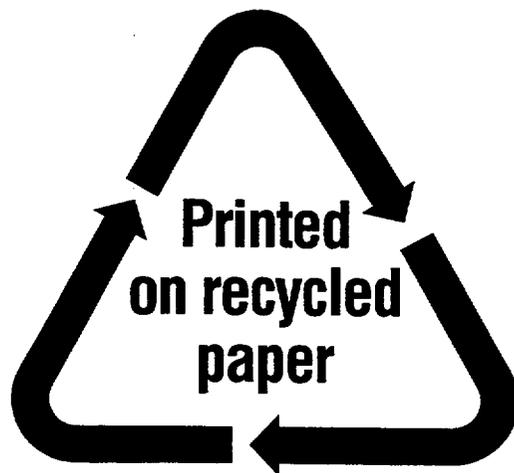
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