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Radiological Characterization of Spent Control Rod Assemblies

Prepared by
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Pacific Northwest Laboratory
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U.S. Nuclear Regulatory Commission

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Abstract

This document represents the final report of an ongoing study to provide radiological characterizations, classifications, and assessments in support of the decommissioning of nuclear power stations. Earlier studies addressed the characterization of residual radionuclide contamination deposited throughout nuclear power stations (Abel, et al., 1986; Robertson, et al., 1991; Robertson, et al., 1993). Later work included the detailed analyses of neutron-activated metal waste (e.g., spent fuel assembly hardware and reactor pressure vessel steel) removed from reactor pressure vessels (Robertson, et al., 1991; Robertson, et al., 1993). This report describes the results of non-destructive and laboratory radionuclide measurements, as well as waste classification assessments, of BWR and PWR spent control rod assemblies which are typical of those being shipped to commercial low-level waste disposal facilities. The BWR spent Control Rod Blade (CRB) was a General Electric cruciform control rod from Duane Arnold Energy Center. The two types of PWR spent control rods were a Westinghouse Rod Cluster Control Assembly (RCCA) and a Burnable Poison Rod Assembly (BPRA), both from Point Beach 1 Nuclear Station. The radionuclide inventories of these spent control rods were determined by three separate methodologies, including 1) direct assay techniques, 2) calculational techniques, and 3) by sampling and laboratory radiochemical analyses. For the CRB and the BPRA, ^{60}Co and ^{63}Ni, present in the stainless steel cladding, were the most abundant neutron activation products. The boron carbide and the borosilicate glass neutron absorption materials contained insignificant radionuclide inventories compared to the stainless steel. The most abundant radionuclide in the RCCA was ^{108m}Ag (130 year halflife) produced in the Ag-In-Cd alloy used as the neutron poison. This radionuclide will be the dominant contributor to the gamma dose rate for many hundreds of years. The results of the direct assay methods, utilizing gamma spectrometry/TLD dosimetry/dose-to-Curie conversions, agreed very well (±10%) with the sampling/radiochemical measurements, thus lending confidence to the presently employed direct assay methodology used by the utilities and vendors for determining Curie contents of neutron-activated metal waste components. The results of the calculational methods agreed fairly well with the empirical measurements for the BPRA, but often varied by a factor of 5 to 10 for the CRB and the RCCA assemblies. Because of the large quantities of neutron poison material in the control rods and the uncertainties in their exact locations relative to the reactor core over their operating histories, it is difficult to accurately calculate the radionuclide inventories in these components. If concentration averaging and encapsulation, as allowed by 10CFR61.55, is performed, then each of the entire control assemblies would be classified as Class C low-level radioactive waste. These studies have provided important information and data relative to the waste disposal considerations associated with nuclear power station decommissioning.

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Executive Summary

This study has been conducted by Pacific Northwest Laboratory (PNL) to provide the U. S. Nuclear Regulatory Commission (NRC) and licensees with a more comprehensive data base and regulatory assessment of the radiological factors associated with the decommissioning of nuclear power stations and the disposal of wastes generated during such activities. This report is the final of a series of NUREG/CR documents which have extended the state of knowledge of the radiological source term conditions existing at nuclear power stations at the initiation of decommissioning operations. Earlier studies addressed the characterization of residual radionuclide contamination deposited throughout nuclear power stations (Abel, et al., 1986; Robertson, et al., 1991; Robertson, et al., 1993). Later work included the detailed analyses of neutron-activated metal waste (e.g., spent fuel assembly hardware and reactor pressure vessel steel) removed from reactor pressure vessels (Robertson, et al., 1991; Robertson, et al., 1993). This report describes the results of non-destructive and laboratory radionuclide measurements, as well as waste classification assessments, of BWR and PWR spent control rod assemblies which are typical of those being shipped to commercial low-level waste disposal facilities. The primary objectives of these characterization studies were: 1) to determine the spectrum of radionuclides produced in various types of spent control rods, 2) assess the accuracy of various direct and indirect methods commonly in use for determining the radionuclide inventories in the control rods, 3) evaluate the waste disposal options for these highly radioactive components, and 4) provide a more comprehensive data base for conducting further decommissioning assessments of nuclear power stations.

During 1992 a unique opportunity became available through the DOE Office of Civilian Waste Programs to obtain samples of spent control rod assemblies for conducting detailed radiological characterization, classification, and assessment of waste disposal options. The radionuclide composition, distributions, and inventories for three types of spent control rod assemblies were determined by both direct assay techniques and by sampling and laboratory radiochemical analyses. These empirical measurements were then compared with the results of calculational methods to determine the accuracy of the calculations.

The three types of spent control rod assemblies, having well-documented irradiation histories, examined in this study included a General Electric BWR Control Rod Blade (CRB) from Duane Arnold Energy Center, a Westinghouse PWR Rod Cluster Control Assembly (RCCA) from Point Beach 1 Nuclear Station, and a Westinghouse PWR Burnable Poison Rod Assembly (BPRA) also from Point Beach 1 Nuclear Station.

The BWR Control Rod Blade, composed of stainless steel cladding tubes with with boron carbide poison, contained predominantly ^{60}Co, which was produced by neutron activation of the nominally 2800 ppm of stable cobalt present in the steel. Nickel-63, ^{93m}Nb, and ^{59}Ni were the next most abundant long-lived activation products, being about 10-fold, 300-fold, and 1000-fold lower, respectively, in concentration compared to ^{60}Co. The ^{94}Nb concentrations averaged about 50-fold lower than those for ^{93m}Nb. The concentrations of the activation products decreased approximately 50-fold from the insert end to the tail end of the neutron-absorbing section of the CRB. The gamma dose rate at the insertion end of the CRB peaked at about 2900 R/h at contact in August, 1990 approximately two years after removal from service. The boron carbide neutron absorber material in the CRB contained relatively low concentrations of all radionuclides, and this material contributed insignificantly to the total radionuclide inventory for the CRB.

The PWR Rod Control Cluster Assembly, composed of stainless steel-clad borosilicate glass, likewise contained predominantly ^{60}Co, produced from the 1600 ppm of cobalt present in the steel. This steel likewise contained similiar amounts of ^{63}Ni, ^{93m}Nb, ^{59}Ni, and ^{94}Nb, relative to the ^{60}Co, as observed in the CRB. The concentrations of the activation products were rather uniformly distributed over the length of the neutron-absorbing section of the BPRA. The gamma dose rate over this section was about 120 R/h at contact in August, 1990, approximately 15 years after removal from service.

The PWR Rod Control Cluster Assembly is composed of stainless steel-clad rods of an alloy made of 80% Ag, 15% In, and 5% Cd for absorbing neutrons. The radionuclide composition of this assembly is unique, in that the most abundant long-lived radionuclide was ^{108m}Ag. Silver-108m has a half-life of 130 years and decays mainly by electron capture accompanied by the emission of three relatively high energy coincident gamma rays (439, 614, and 722 keV) each of 91% relative intensity. On a per gram basis, the concentration of ^{108m}Ag in this alloy is comparable to the ^{60}Co concentrations in the stainless steel cladding, but the mass of the Ag/In/Cd alloy greatly exceeds that of the stainless steel cladding. Therefore, the ^{108m}Ag will be the dominant gamma dose-contributing radionuclide in this type of control rod assembly for many hundreds of years. Silver-108m is not addressed in 10CFR61, so it cannot be considered in waste classification assessments for this assembly. The RCCA was fully withdrawn at all times

during full power operations and only the first few tens of cm on the insertion end of the RCCA were highly neutron activated. The gamma dose rate at the insertion end peaked at about 290 R/h at contact in August, 1990, approximately 10 years after removal from service.

It was possible to directly compare radionuclide measurements for several activation products (^{60}Co, ^{63}Ni, ^{59}Ni, and ^{94}Nb) with samples taken from approximately the same locations on the rod assemblies by another group at PNL (Miglion, et al., 1994). The results of this intercomparison were very good, with general agreement being in the range of 1-25%, except for ^{94}Nb where our results averaged about 23 times higher.

Direct assay measurements of the three spent control rod assemblies were conducted in the hot cell facilities at PNL. This technique, which was described in detail in Robertson, et al. (1993), consists of: 1) direct gamma ray spectrometry to identify those radionuclides contributing to the gamma dose rate, 2) thermoluminescent dosimetry (TLD) to measure the gamma dose rate along the length of the control rod, 3) dose-to-Curie conversion using appropriate shielding/geometry codes, and 4) correlations (scaling) to the ^{60}Co to estimate the concentrations of other 10CFR61 radionuclides in the assemblies. The results of the direct assay measurements were only 10% lower than the empirical measurements for the CRB and the BPRA. The laboratory value for ^{108m}Ag, which was the most abundant radionuclide in the RCCA and contributed to most of the gamma dose, was only 2% higher than the direct assay results, but the ^{60}Co and ^{110m}Ag laboratory values for the RCCA were a factor of 2.8 higher than the direct assay results. This generally good agreement between the laboratory versus the direct assay measurements of the radionuclide contents of spent control rod assemblies lends confidence that the direct assay methodologies can provide very accurate determinations of the radionuclide inventories of spent control rod assemblies and other types of highly neutron-activated metal wastes.

Calculated radionuclide inventories for these spent control rod assemblies were also determined by a reactor physics group at PNL using both ORIGEN2 and MCNP modeling, and their results were compared with our laboratory measurements. Neutronics modeling calculations are especially difficult to perform for spent control rod assemblies because of the large quantities of neutron absorbing materials in the rods and the uncertainties in their exact position relative to the reactor core over their operational history. The objective of this comparison was to determine how accurate the calculations were relative to the laboratory measurements (assumed to be the more accurate of the two methods). This comparison showed that for the CRB our laboratory values for ^{60}Co, ^{63}Ni, and ^{59}Ni were about 3 to 5 times higher than the calculated values at the insert ("hot") end of the assembly, and at the "cold" end of the assembly our laboratory values were 0.15 to 0.68 times the calculated values. For the BPRA, our laboratory ^{60}Co values were 3.9 times higher than the calculated values, and the laboratory ^{63}Ni and ^{59}Ni values were 0.78 and 0.73 times the calculated values. For the insert end of the RCCA, our laboratory ^{60}Co, ^{63}Ni, and ^{59}Ni values were 3.6, 12.7, and 12.6 times higher, respectively, than the calculated values. These comparisons confirm the difficulty in calculating the radionuclide inventories in spent control rod assemblies. It appears that generally it is possible to perform radionuclide inventory calculations that are within a factor of about 5 of the true values, but occasionally, differences exceeding a factor of ten were observed. Obviously, the direct assay techniques are preferable to the calculational methods for estimating radionuclide inventories of spent control rod assemblies.

The radionuclide inventories of the three spent control rod assemblies were assessed to provide a 10CFR61 waste classification of these materials. If concentration averaging over the entire assemblies is performed, as allowed in 10CFR61.55, then each of the assemblies would be classified as Class C low-level waste, even though the "hot" ends of the CRB and BPRA approached or slightly exceeded the Class C limit. Nickel-63, followed by ^{94}Nb, were the classification-controlling radionuclides. Since the concentrations of these radionuclides are so close to the Class C limit for the these types of activated-metal waste it is important that the determination of their radionuclide contents be determined as accurately as possible.

The information and data bases that have been generated during these radionuclide characterization studies have provided a more comprehensive and reliable assessment of the radiological factors associated with the decommissioning of nuclear reactor power stations.

Foreword

This document is the final report of a study to provide radiological characterizations, classifications, and assessments in support of the decommissioning of nuclear power stations. This document describes the results of non-destructive and laboratory radionuclide measurements, as well as waste classification assessments, of BWR and PWR spent control rod assemblies which are typical of those being shipped to commercial low-level waste disposal facilities. The information contained in this report is used by the NRC to help develop rules and guidance relative to radioactive waste disposal and reactor decommissioning.

This report is not a substitute for NRC regulations, and compliance is not required. The approaches and/or methods described in this report does not necessarily constitute NRC approval or agreement with the information cited herein.

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1 Introduction

1.1 Project Plan and Objectives

The U.S. Nuclear Regulatory Commission (NRC) has enacted rules setting forth technical, safety, and financial criteria for decommissioning of licensed nuclear facilities, including commercial nuclear power stations (53 FR 24018-56). These rules have addressed five major issues; decommissioning alternatives, timing, planning, financial assurance, and environmental review. Also, the rules governing disposal of low-level radioactive wastes in commercial shallow land burial facilities will be applicable to most of the wastes generated during reactor decommissioning (10 CFR 61). The appropriate response to each of these issues by the licensee and the NRC depends greatly on an accurate and reliable assessment of the residual radiological conditions existing at the nuclear power stations at the time of decommissioning. Large volumes of data exist which describe the radionuclide concentrations associated with active waste streams generated at nuclear power stations. However, comparatively little information has been available that documents the residual radionuclide concentrations, distributions, and inventories residing in contaminated piping, components, and materials of nuclear power plant systems, and in neutron-activated materials associated with the reactor pressure vessel and biological shield. Especially lacking was a detailed radiological characterization of the numerous types of wastes encountered during an actual reactor decommissioning and a characterization of the highly neutron-activated metal components associated with pressure vessel hardware, spent fuel assembly hardware, and spent control rods and control assemblies.

Pacific Northwest Laboratory (PNL)[1] has conducted this study to provide the NRC and licensees with a more comprehensive data base for regulatory assessment of the radiological factors associated with reactor decommissioning and disposal of wastes generated during these activities. This final phase of the study has focused on the radionuclide characterization of dismantled neutron-activated components from commercial power reactors, e.g. spent control rod assemblies from a BWR and a PWR station. This work has addressed the following objectives:

- radiological characterization and classification of intensely radioactive materials removed from the reactor pressure vessel, including spent control rod assemblies from commercial nuclear power plants
- evaluation of the accuracy of direct assay techniques and computer code calculations for estimating/predicting radionuclide inventories in retired reactors and neutron-activated components
- assessment of waste disposal options associated with reactor decommissioning.

1.2 Scope of Study

This final phase of the study has focused on the characterization and classification of in-core reactor components which will be part of the intensely radioactive waste materials derived from nuclear reactor decommissioning. Earlier studies in this work addressed the characterization of residual radionuclide contamination deposited throughout nuclear power stations (Abel, et al., 1986; Robertson, et al., 1991; Robertson, et al., 1993). Later work included the detailed analyses of neutron-activated metal waste (e.g., spent fuel assembly hardware and reactor pressure vessel steel) removed from reactor pressure vessels (Robertson, et al., 1991; Robertson, et al., 1993). This final phase involved non-destructive and laboratory radionuclide measurements, as well as waste classificaton assessments, of one BWR and two PWR spent control rod assemblies which are typical of those being shipped to commercial low-level waste disposal facilities. The scope of these characterization studies involved: 1) determination of the spectrum of radionuclides produced in the three types of control rod assemblies, 2) assessment of the accuracy of various direct and indirect methods commonly in use for determining the radionuclide inventories in the control rods, 3) evaluation of the waste disposal options for these highly radioactive waste components, and 4) providing a more comprehensive database for conducting further decommissioning assessments of nuclear power stations.

1.3 Waste Disposal Options for Neutron Irradiated Components Associated with Reactor Decommissioning

The rule governing disposal of low-level radioactive wastes in shallow land burial facilities (10 CFR 61) will have direct impact on the options available for disposal of highly radioactive components of decommissioning wastes. Previous studies by Smith et al. (1978) and Oak et al. (1980) have indicated that all primary, secondary, and auxiliary systems in a nuclear power plant would probably have residual radionuclide contamination levels sufficiently low

[1]Pacific Northwest Laboratory is operated for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

to permit disposal as Class A waste. The Shippingport Station decommissioning provided an excellent opportunity to test and confirm these previous observations (Robertson, et al., 1991).

The waste disposal options for highly radioactive neutron-activated metal components associated with spent fuel assembly hardware from PWR and BWR stations were previously evaluated (Robertson, et al., 1991; Robertson, et al., 1993). It was demonstrated that the ^{59}Ni, ^{63}Ni, and ^{94}Nb concentrations in these materials classified them in the greater-than-Class C category.

This present study has provided, for the first time, detailed measurements and classification of the long-lived neutron activation products in a spent BWR control rod blade and in two PWR control rod assemblies. These control rods were sampled and detailed radiochemical analyses of both cladding and neutron absorber materials were performed. The waste classification of these materials was then determined and disposal options considered.

1.4 Background Information

During the late 1970s and early 1980s, Pacific Northwest Laboratory conducted a number of studies for the NRC to assess the technology, safety, and costs associated with reactor decommissioning (Smith, et al., 1978; Oak, et al., 1980; Wittenbrock,1982; Murphy and Holter, 1982; Konzek, et al., 1982). These studies were based on extremely limited radionuclide source terms for residual radioactivity within a retired nuclear power plant. To fill this data gap, the NRC sponsored two research projects to provide a detailed database describing the residual radionuclide concentrations, distributions, and inventories within retired nuclear power stations (Abel, et al., 1986; Robertson, et al., 1984; Evans, et al., 1984; Evans, et al., 1988). These projects characterized the neutron activation products formed in reactor pressure vessels and their internal components, and the residual surface contamination spread to all other systems and areas of the station. Although these studies greatly strengthened the radionuclide source term information on residual radioactivity in nuclear power stations, several major data gaps were further identified. These consisted of a lack of detailed radiological characterization data during an actual reactor decommissioning and a lack of radionuclide contents of neutron activated metal components from within reactor pressure vessels.

This program has conducted research to address these important areas of reactor decommissioning. The Shippingport Station decommissioning provided a detailed radiological characterization during the dismantlement and decommissioning of a nuclear power station (Robertson, et al., 1991, Robertson, et al., 1993). In addition, specimens of spent fuel assembly hardware and pressure vessel components were analyzed to determine their radionuclide contents for waste disposal considerations.

This present report discusses the results of detailed radiological characterization of spent control rod assemblies. The spent control rod assemblies were analyzed to determine radionuclide contents, waste classification, disposal options, and the degree of accuracy of calculational methodology for predicting the concentrations of neutron-activated products in irradiated metal components. The results of this source term characterization work will provide for more accurate and reliable assessments of the technology, safety, and costs of reactor decommissioning.

2 Description of Spent Control Rod Assemblies

A wide variety of neutron-activated metal wastes, including spent control rods and assemblies, are being generated in increasing quantities at both operating and decommissioned nuclear power stations throughout the world. These wastes, which originate from within the reactor pressure vessel, have normally been exposed to very high neutron fluences and subsequently have extremely high dose rates (thousands of R/h). Before disposal, the radionuclide contents of these wastes must be measured to determine the waste classification, packaging requirements, and shipping regulations. The very high dose rates associated with these components greatly complicate the sampling and radionuclide analyses that must be performed. Usually activation modeling calculations or remote, direct assay techniques have been employed to determine the Curie contents of these wastes (Cline, et al., 1987). The reliability and accuracy of these calculational and direct assay methods need to be further demonstrated. This verification can only be accomplished by careful sampling and laboratory analysis of the radionuclides of interest and their stable parent elements in the waste metal components, and by comparing these measurements with the results of the calculations and direct assays performed on the same activated metal waste components.

2.1 Description of Spent Control Rods

Three types of spent control rod assemblies with well-documented irradiation histories (see Migliore, et al., 1994) have been made available for sampling and radiological characterization at PNL through the U.S. Department of Energy's Office of Civilian Radioactive Waste Management. These components are also being utilized in this NRC project to compare and assess the three main methods of characterizing the radionuclide contents of highly neutron-activated metal wastes: 1) sampling and laboratory analyses, 2) direct assays, and, 3) calculational methods. In addition, these measurements will provide important information concerning waste classification and disposal requirements. The three different types of spent control rods examined in this study are listed in Table 2.1, and include a BWR Control Rod Blade (CRB), a PWR Rod Cluster Control Assembly (RCCA), and a PWR Burnable Poison Rod Assembly (BPRA).

2.1.1 Description of BWR Control Rod Blade (CRB)

The CRB was obtained from a General Electric BWR station operated by Iowa Light and Power Company at the Duane Arnold Energy Center. The CRB is predominantly stainless steel, and inside each blade are stainless steel tubes that are filled with boron carbide (B_4C) powder which acts as a neutron absorbing material. The absorbing section of the blade is cruciform shaped. At the bottom of the blade is a circular velocity limiter and the overall length is about 14 feet. Figure 2.1 is a schematic representation of the BWR CRB, showing the sampling locations, DER-1, DER-2, and DER-3. Details of the sampling are given in Section 4.

The irradiation history of this control rod is described by Migliore, et al., (1994). This CRB was exposed to 10 operating cycles and discharged in October 1988. It was inserted to various levels in the core during its exposure, but the exposure of the blade during full power was very low since the reactor would be either coasting down or at zero

Table 2.1 Spent Control Rod Assemblies for Radiological Characterization

Assembly Type	Discharge Date	Reactor Station	Materials Sampled
BWR Control Rod Blade (CRB) ID No. AR-0054R	10/88	Duane Arnold Energy Center	Stainless steel, B_4C
PWR Rod Cluster Control Assembly (RCCA) ID No. R03	4/85	Point Beach 1 Nuclear Station	Stainless steel, Ag/Cd/In alloy
PWR Burnable Poison Rod Assembly (BPRA) ID No. 4P5	11/75	Point Beach 1 Nuclear Station	Stainless steel, B glass

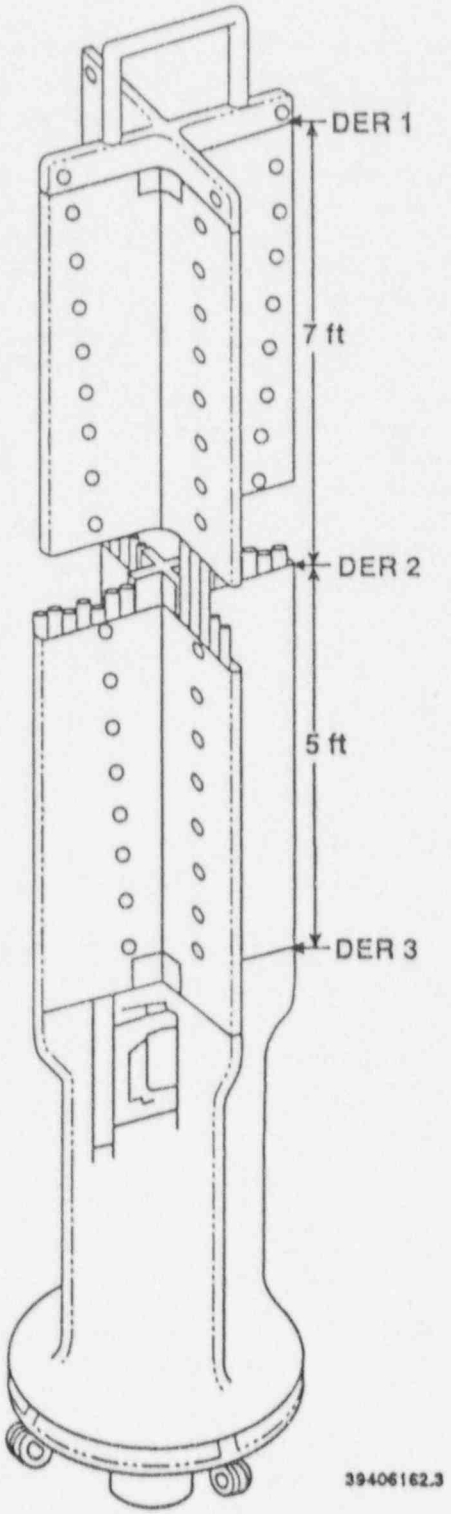

Figure 2.1 Schematic of BWR Cruciform Control Rod Showing Sampling Locations DER-1, DER-2, and DER-3.

power level when it was fully inserted. A measure of the exposure of the CRB is given in Table 2.2 where absorber depletion is tabulated.

The stellite (high Co alloy) bearing section of the control rod was removed at the power station because of the extremely high dose rate due to ^{60}Co in this component. The material sampled and analyzed included the stainless-steel cladding, as well as the stainless-steel tubes that contained the boron carbide material that acts as a neutron absorber.

Table 2.2 Depletion of Boron-10 in Control Rod Blade*

Quarter	Snvts**	% Depletion
1 (top)	1.85	30.73
2	1.91	31.69
3	1.46	21.16
4 (bottom)	0.48	7.98

* From Migliore et al., 1994.
** The units "Snvts" is a term used to denote 10^{21} n/cm^2. It is a measure of the total irradiation the CRB has experienced and is correlated to the percent depletion of boron-10.

2.1.2 Description of Rod Cluster Control Assembly (RCCA)

The RCCA was obtained from a Westinghouse designed PWR operated by Wisconsin Electric at Point Beach 1 Nuclear Station. The RCCA is constructed from stainless steel and is approximately 14 feet long. There are 16 rods that are attached to the top of the assembly. Figure 2.2 is a schematic of a PWR RCCA showing sampling locations DER-7, DER-8, DER-9, and DER-10. The RCCA is of special interest, not only because of the stainless-steel cladding, but because of the solid rod of silver-indium-cadmium alloy (80% Ag, 15% In, and 5% Cd) used as a neutron absorber. The silver and cadmium can both produce long-lived neutron activation products (^{108m}Ag and ^{113m}Cd) that may be of significance from a waste-management perspective. The RCCA was designed to fit into a 14 X 14 fuel lattice.

The RCCA was exposed to 12 operating cycles and 102,767 hours of critical reactor service. It was discharged in April 1985. Migliore, et al. (1994) indicate that the RCCA was fully withdrawn at all times during full power operations. The reactor had an output of 1500 MWt and the assembly burnup was 125,589 Mwd/MTU.

2.1.3 Description of Burnable Poison Rod Assembly (BPRA)

The BPRA was also obtained from the Point Beach 1 Nuclear Station. This is a PWR control rod assembly designed by Westinghouse. It also is about 14 feet long and constructed primarily from stainless steel. The top of the assembly includes the hold-down bar and spring. Attached to the hold-down assembly are four burnable poison rods and 12 thimble plugs. The thimble plugs are constructed of solid stainless steel while the poison rods are filled with borosilicate glass for neutron absorption. Figure 2.3 is a schematic of the BPRA. The BPRA is of interest because of the stainless-steel cladding, the solid stainless-steel thimble plugs, and the four burnable poison rods which contain cylindrical tubes of borosilicate glass to act as a burnable neutron absorber.

The exposure history of the BPRA is detailed by Migliore, et al. (1994). It was irradiated during Cycle 3 in position E-22 and discharged November 16, 1975.

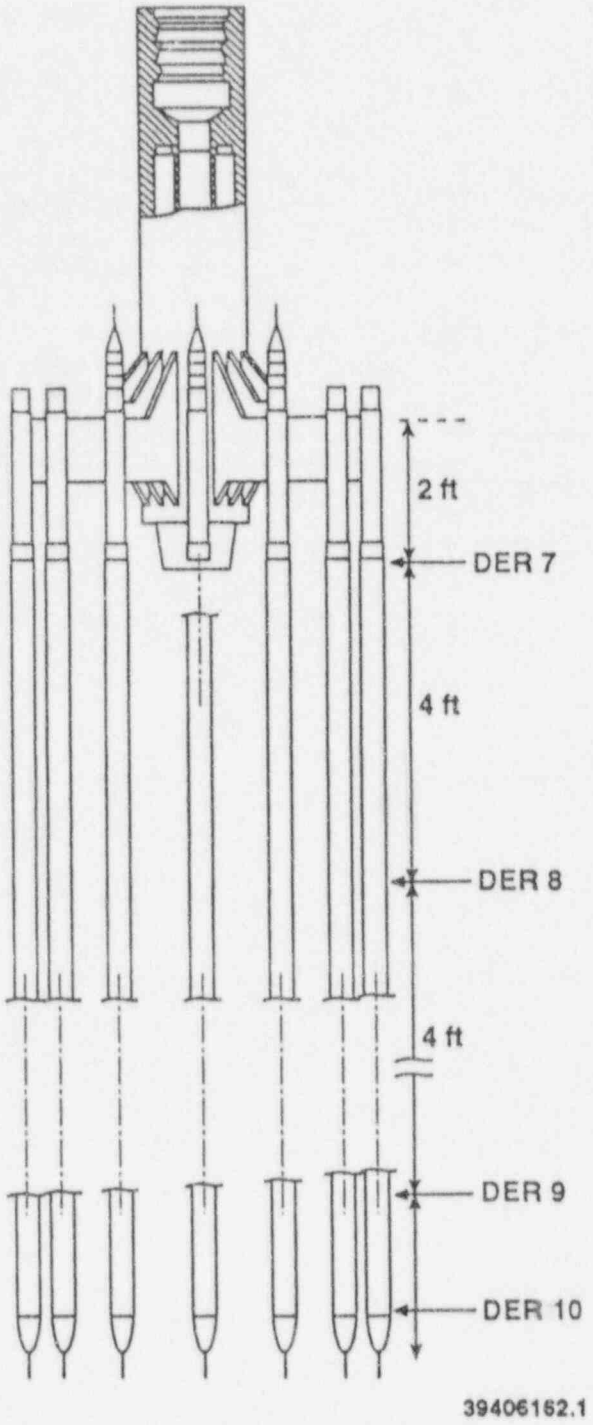

Figure 2.2 Schematic of PWR Rod Cluster Control Assembly (RCCA) Showing Sampling Locations DER-7, DER-8, DER-9, and DER-10.

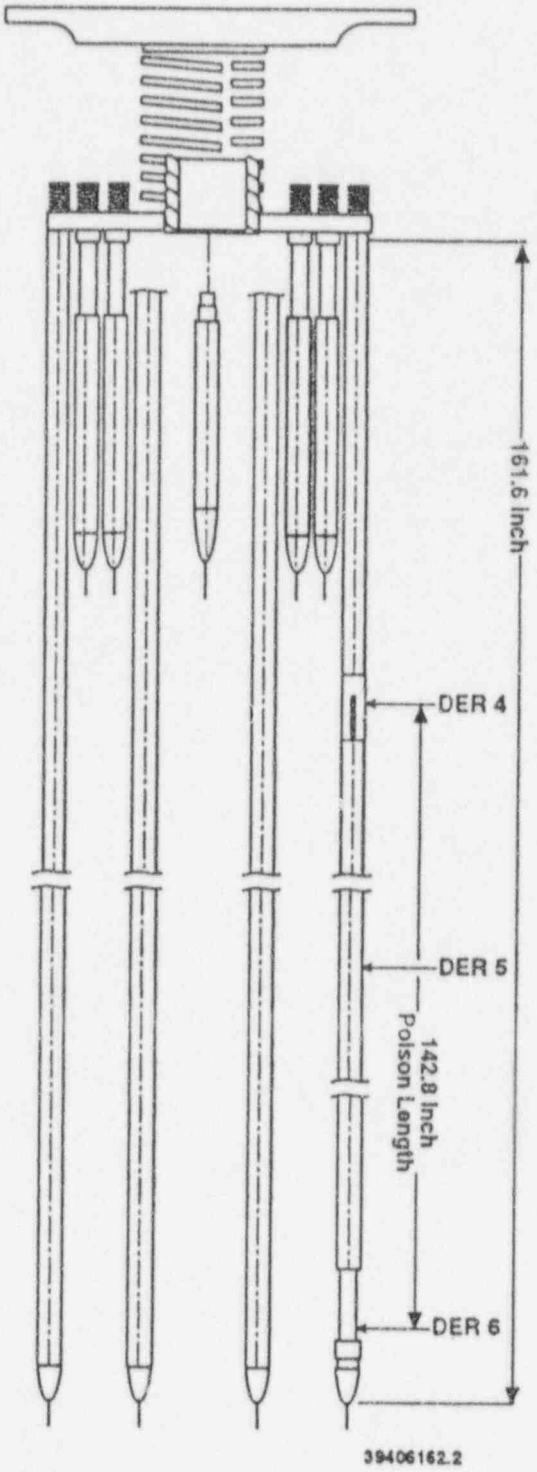

Figure 2.3 Schematic of Burnable Poison Rod Assembly (BPRA) Showing Sampling Locations for DER-4, DER-5, and DER-6

3 Description of Direct-Assay Methods to Determine Curie Content

Two direct-assay methods have been employed to determine the Curie contents of the neutron-activated metal components of the spent control rod assemblies. The direct-assay techniques are powerful tools that can be used to determine the radionuclides specified in 10 CFR 61 for activated metal wastes, especially high-activity components such as spent control rods because of their very high dose rates (thousands of R/h). Various adaptations of the dose-to-Curie conversion technique are used by the nuclear utilities and vendors, in which measured dose rates are converted into radionuclide inventories using shielding/geometry codes and correlation analyses.

3.1 Gamma Spectrometry and Dose-to-Curie Conversions

The first method to be described employs gamma spectrometry and dose-to-Curie conversion codes to determine the Curie content of the control rods. The technique involves the following steps: 1) gamma-ray spectrometry for qualitative analysis; 2) thermoluminescent dosimetry (TLD), followed by accurate dose-to-Curie conversion using appropriate shielding codes; and 3) correlation analysis for estimating the concentrations of non-gamma-emitting isotopes. This methodology is described in detail by Robertson, et al. (1993).

The gamma spectrometry for qualitative analysis was performed on the control rods in the 324 Building Hot Cell. Figure 3.1 is a schematic of the setup used to scan the control rods. A 1.3 cm diameter steel collimator tube was installed through the 1.5 m thick concrete wall of the hot cell. A portable intrinsic germanium gamma-ray detector was positioned at the outside end of the collimator, and the control rods were hoisted vertically past the inside end of the collimator to provide a vertical profile of the gamma-ray spectra along the length of each of the control rods. In the case of the BWR control rod, it was located almost 6 m away from the detector when the profile scans were obtained. For the BWR Control Rod Blade and the PWR Burnable Poison Rod Assembly, ^{60}Co was the predominant radionuclide contributing to the gamma-ray spectra, with a trace of ^{54}Mn also being present. For the PWR Rod Cluster Control Assembly, the predominant radionuclides in the gamma-ray spectrum were ^{108m}Ag, ^{110m}Ag, and ^{60}Co, in that order.

Next, dose-rate profiles were obtained by placing a string of TLD's along the length of each control rod for a short period of time (typically 10 to 30 min). The TLD's were then retrieved and read. The gamma-dose-rate information along with the gamma spectrometry data were then used as input to the shielding codes (for example, MCNP - Monte Carlo Neutron and Photon transport code) to convert the dose rates into Curie contents. Once this information had been obtained for the dominant gamma-ray emitting radionuclides, the balance of the radionuclides specified in 10 CFR 61 were calculated using correlation analysis (Robertson, et al., 1993).

The computed activity content of ^{60}Co for the BWR Control Rod Blade as a function of TLD sample location is shown in Figure 3.2. A total Curie content for ^{60}Co was calculated to be 271 Ci (on August 17, 1990).

3.2 Integral Dose Method

A second method, called the Integral Dose Method, was also used to determine the Curie content of the spent control rod assemblies. The measured dose rate at each TLD location along the length of the control rod is summed to give a total integrated dose for the entire control rod. The integrated dose is then converted to ^{60}Co content by applying standard dose-to-Curie conversion factors. The gamma spectrum is also used to determine the major gamma-emitting radionuclides present that would be contributing to the dose observed by the TLD's. This information is then input into an activity code that calculates the ^{60}Co concentration at the time of removal from the reactor and then calculates the Curie concentrations of the 10CFR 61 radionuclides at any date specified. Using this method, a total ^{60}Co Curie content of 282 Ci was measured for the CRB.

3.3 Results of the Two Direct Assay Methods

The results of the two direct assay methods are listed in Table 3.1. Excellent agreement was obtained for the PWR Rod Cluster Control Assembly (RCCA) between the MCNP method and the Integral Dose method. In fact, there was only a 1.0% difference between the Curie contents calculated by the two methods. The agreement between the two techniques was still quite good for the BWR Control Rod Blade (CRB). There was only a 3.9 % difference between the two techniques. The largest disagreement was obtained for the PWR Burnable Poison Rod Assembly (BPRA) at 12.6% difference between the MCNP results and the Integral Dose method results.

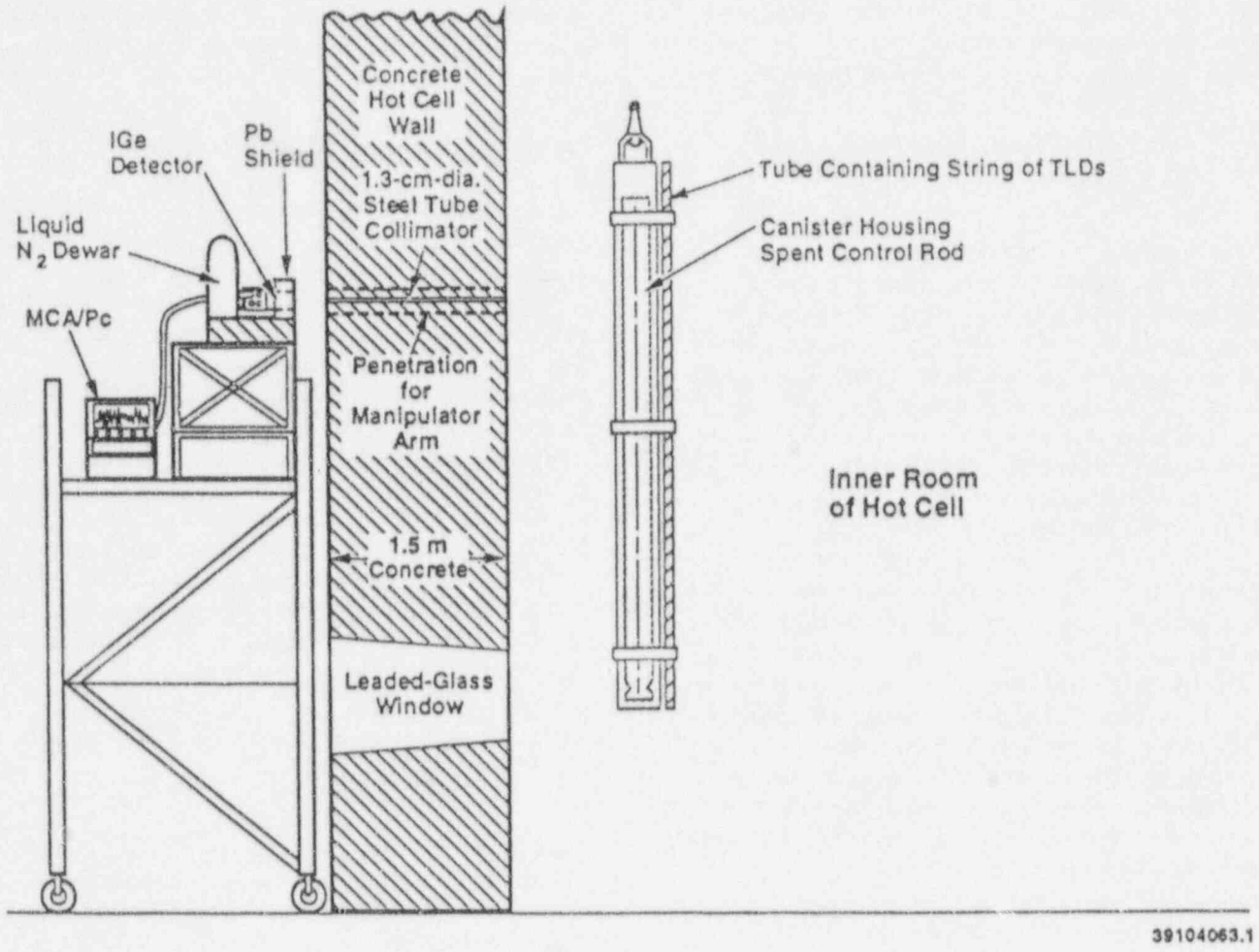

Figure 3.1 Schematic Elevation View of Collimator System for Direct Gamma-Ray Spectrometry of Spent Control Rods

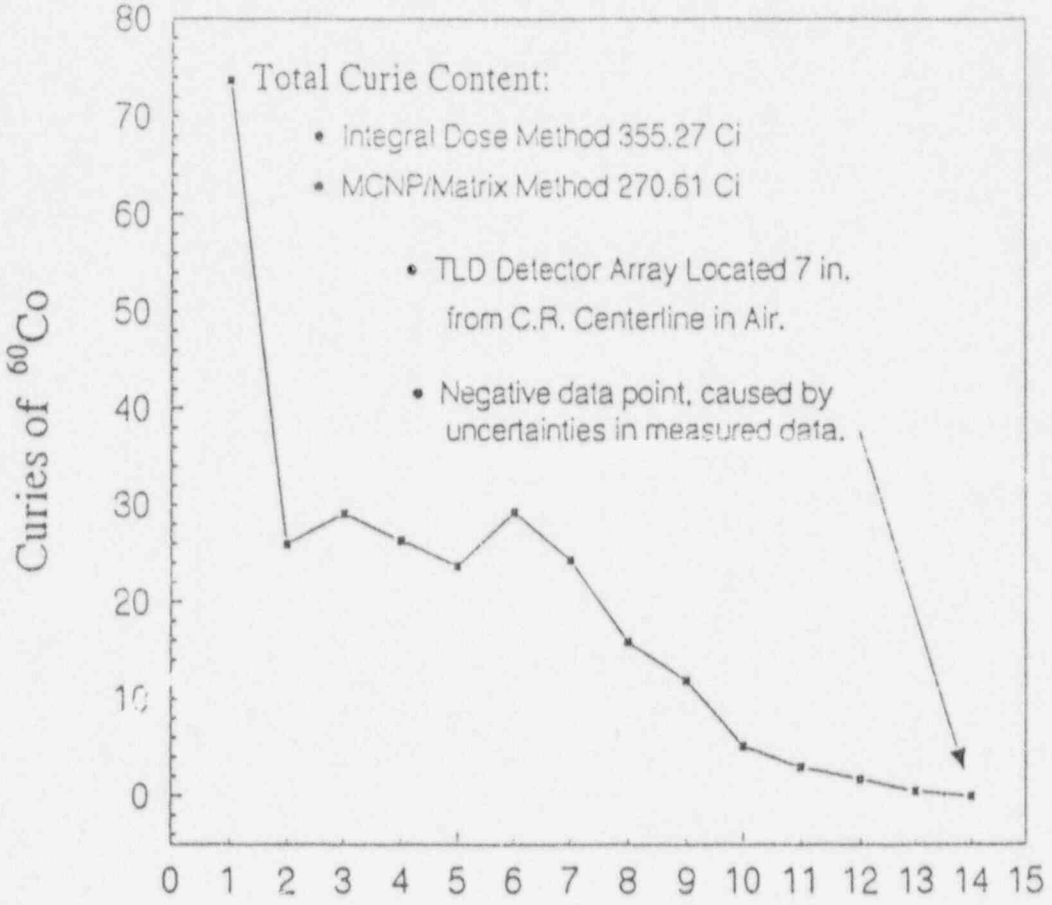

Figure 3.2 Cobalt-60 Distribution and Content of CRB (August 17, 1990).

Table 3.1 Curies of ^{60}Co Measured by Two Direct Assay Techniques in Spent Control Rods*

Control rod	MCNP method	Integral dose	% difference
BWR Control Rod Blade	271	282	3.9
PWR Burnable Poison Rod Assembly	32.6	37.3	12.6
PWR Rod Cluster Control Assembly	19.6**	19.8**	1.0

* Activity as of 8/20/90

** Includes 3.4 Ci ^{60}Co, 9.6 Ci of ^{108m}Ag, 6.7 Ci of ^{110m}Ag

4 Radiological and Stable Element Characterization of Control Rod Samples

4.1 Description of Samples Obtained for Radiochemical Analysis

Actual samples of each control rod were obtained by cutting small specimens from the control rod using remote handling equipment. This work was done in the 324 Building Hot Cells because of the high dose rates associated with these control rods. For this project, typically three samples were obtained from each control rod, one at each end and one from the middle. This sampling has been described in more detail by Migliore, et al. (1994). Using the schematic of each control rod and knowing our sample number (Figures 2.1, 2.2, and 2.3), the corresponding sample obtained by Migliore, et al., may be determined.

Figure 2.1 shows the physical locations for the samples obtained from the BWR Cruciform Control Rod Blade. Each of the three samples consisted of four to six stainless-steel tubes that were surrounded by the stainless-steel cladding of the cruciform control rod blade. The stainless steel tube samples were labeled "a" through "f" where up to six of the tubes were recovered from a blade, and the outside steel cladding over the tubes was labeled "z" cladding. Each stainless-steel tube contained compacted boron-carbide powder that served as a neutron poison. Figures 4.1 and 4.2 are pictures of the gross samples obtained for DER-2 and DER-3, respectively. Note the U-shaped stainless steel cladding that held the stainless steel tubes.

Figure 2.2 shows the sampling locations for the RCCA. In addition to the three samples DER-7, -8, and -9, an additional sample labeled DER-10, which was located at the most radioactive end of the rod, was obtained. These samples consisted of the stainless-steel cladding (Figure 4.3) and the solid Ag-In-Cd alloy rod (Figure 4.4). A sample of the stainless steel plug (Figure 4.5) on the end of the rod (labeled RCCA-8, right next to DER-10) was also obtained for radiochemical analysis.

Figure 2.3 shows the sampling locations for the three samples obtained from the BPRA. The samples consisted of an outer stainless-steel tube (cladding) and an inner stainless steel tube (cladding) with a cylindrical tube of borosilicate glass between the two metal layers. These samples were labeled DER-4, DER-5, and DER-6.

4.2 Description of Sample Preparation for Radiochemical and Stable Element Analysis

The activated metal samples were then transferred to the 325 Building Hot Cell where the individual specimens were separated into their components as much as possible. That is, for the CRB samples, the boron carbide was separated from the individual tubes. Because of the sample handling and looseness of the boron carbide powder, it was not possible to maintain the identity of the boron carbide relative to the tube that it came from. The boron carbide was collected into one composite aliquot for each sample. The stainless steel tubes were separated from the stainless steel cladding that provided the framework for the CRB. Each tube was identified with a letter designation which increased moving from the interior of the CRB to the outer edge of the blade. A small aliquot of the cladding was also obtained for analysis. For the RCCA, the stainless steel cladding was separated from the inner Ag-In-Cd rod in the 325 Building Hot Cells.

The specimens were partially decontaminated at this point by repeated acid etching and then transferred to the 329 Building for final decontamination and/or additional subsampling. The specimens from the CRB consisted of the stainless steel cladding, stainless steel cylindrical tubes, and the boron carbide powder. The specimens for the RCCA consisted of the stainless steel cladding and the solid rod of Ag-In-Cd alloy. The BPRA specimens required additional preparation in the 329 building. The cylindrical tube of borosilicate glass was separated from the inner and outer stainless-steel tubes.

The metal samples were further cleaned by repeated acid rinsing. First, the sample surfaces were cleaned to remove any fission product and activation product debris from their handling in the hot cells. This was determined by monitoring the activity of ^{137}Cs for each acid rinse solution. Once it was determined that the surfaces of the metal specimens had been completely decontaminated from hot-cell debris (by the absence of ^{137}Cs in the rinse solutions), a known amount of each metal specimen was dissolved in acid. Liquid aliquots of the parent solution were then taken for analysis by gamma-spectrometry, stable element analysis by ICP/MS, and analysis of non-gamma-emitting radionuclides by radiochemical separation techniques.

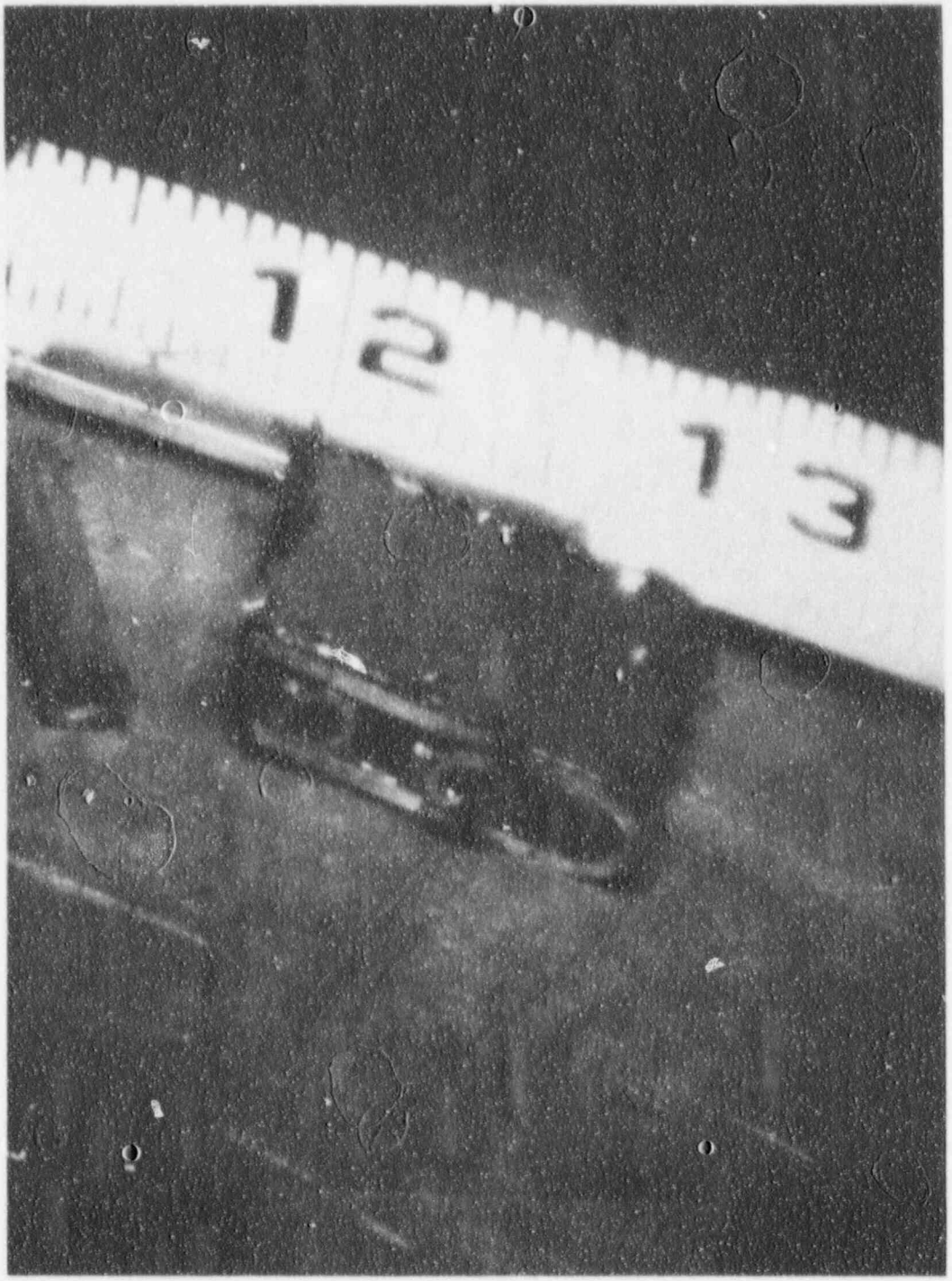

Figure 4.1 Photo of Sample DER-2 from the CRB.

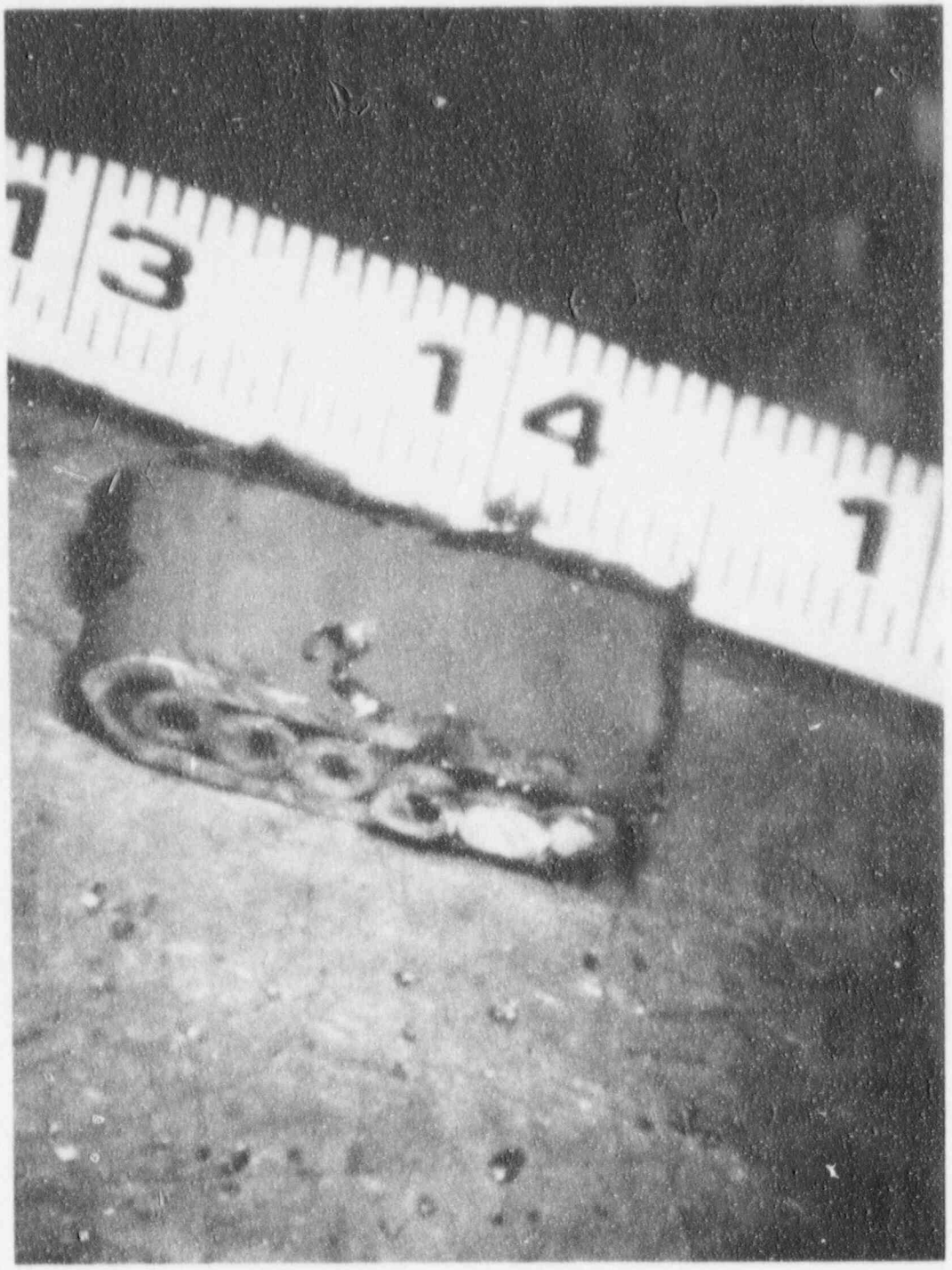

Figure 4.2 Photo of Sample DER-3 from the CRB.

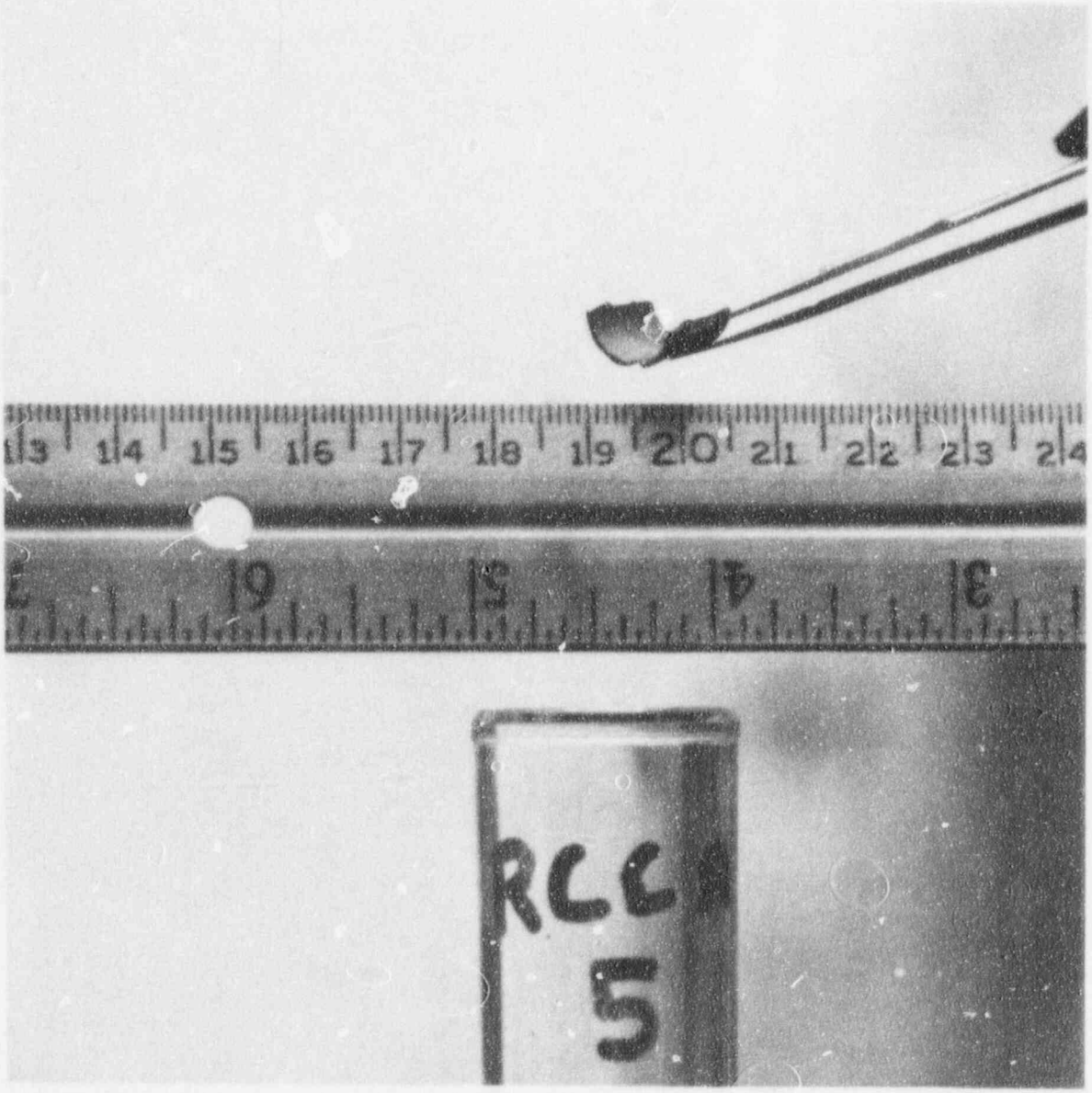

Figure 4.3 Photo of Stainless Steel Cladding for Sample RCCA-5 (similar to DER-8) from the RCCA.

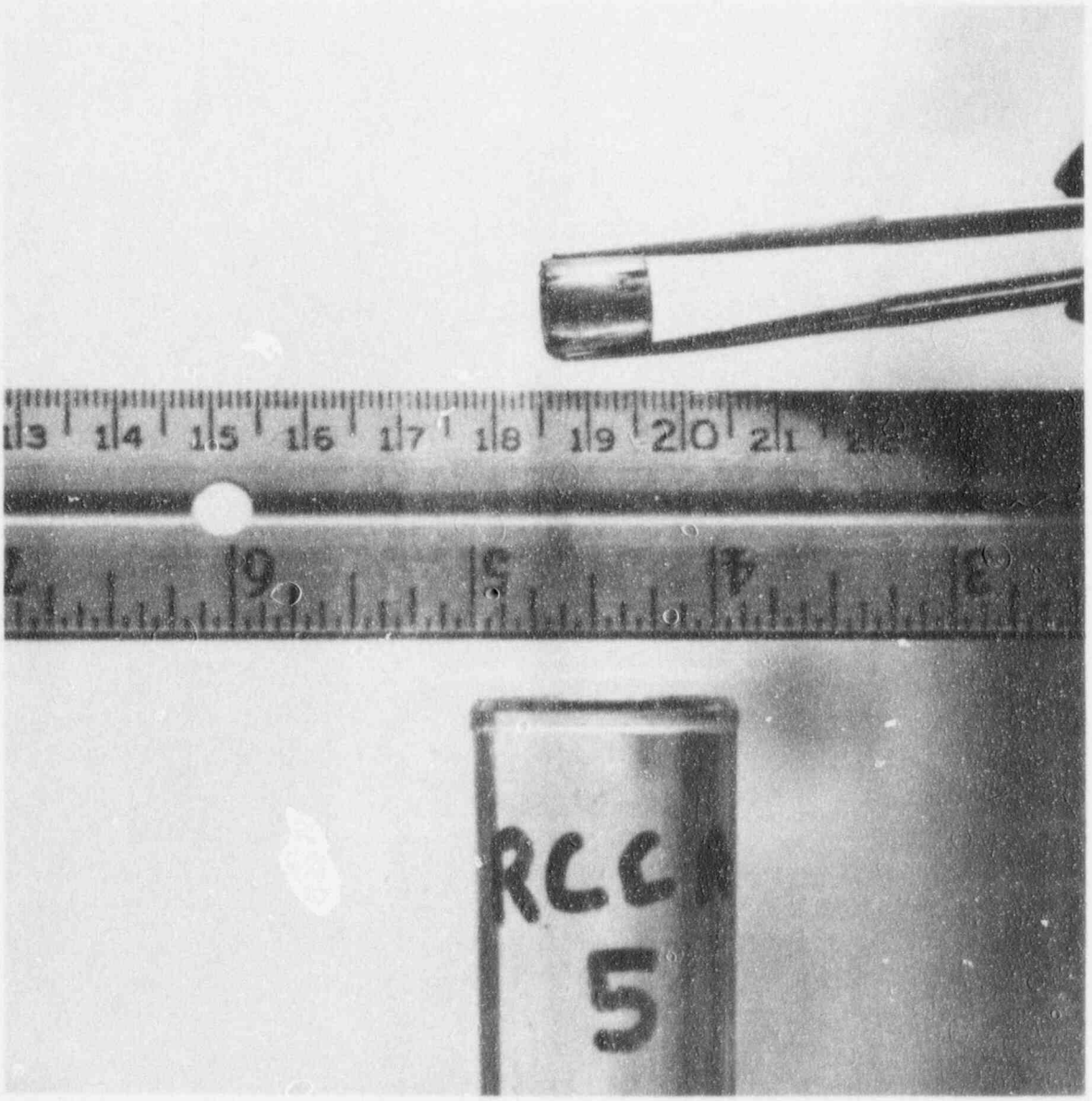

Figure 4.4 Photo of Ag-In-Cd Rod taken from Sample RCCA-5 (similar to DER-8) from the RCCA.

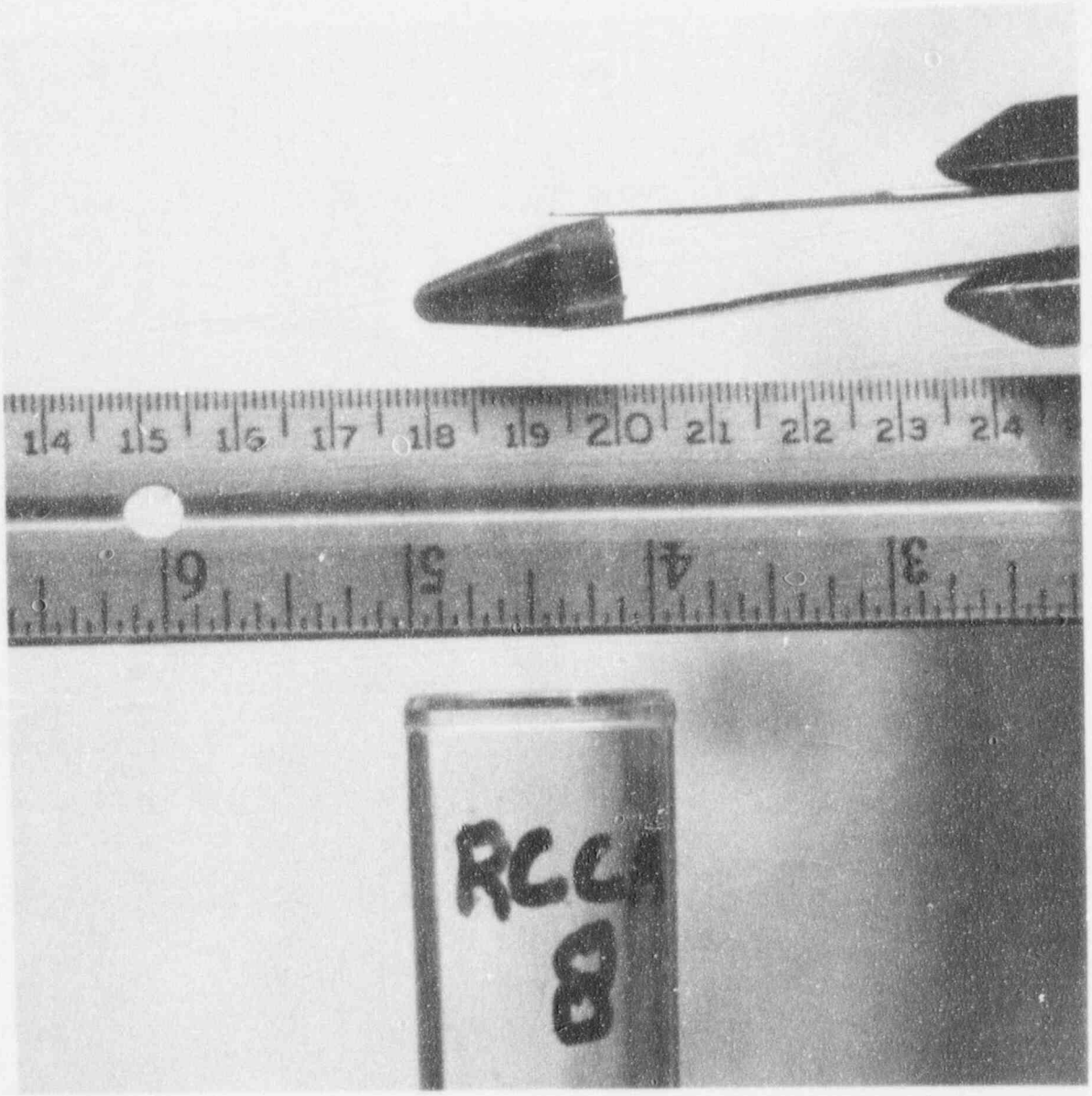

Figure 4.5 Photo of Stainless Steel End Cap for Sample RCCA-8.

4.3 Instrumental and Radiochemical Analysis

Instrumental and radiochemical analyses were performed on the various samples obtained from the three control rods.

4.3.1 Analysis of Metal Samples from the Control Rods

The instrumental gamma spectrometric analysis was performed by obtaining known aliquots of the dissolved solutions from each metal sample and diluting it to 10 mL in a plastic scintillation vial. The radionuclide contents of these sample aliquots were then measured by gamma-ray spectrometry following the procedure described in Lepel (1990). A lithium-drifted germanium detector (14.3% efficient, 76 cc volume, 1.9 keV FWHM for the 1332.5 keV line of ^{60}Co) that was coupled to a Nuclear Data multichannel analyzer was used for these analysis. The spectra were then transferred to a DEC PDP 11/44 computer for data analysis using the RAYGUN code (Hensley, et al., 1988) and storage on magnetic media. The following isotopes were measured in the metals: ^{54}Mn and ^{60}Co, plus ^{108m}Ag, ^{110m}Ag, ^{152}Eu, ^{154}Eu, and ^{155}Eu in the Ag-In-Cd rods.

Radiochemical separation methods were used to measure ^{59}Ni, ^{63}Ni, ^{93m}Nb, ^{94}Nb, and ^{93}Mo in the metal specimens, as well as ^{109}Cd and ^{113m}Cd in the Ag-In-Cd rods. These radiochemical procedures are described in Appendix A.

4.3.2 Analysis of the Borosilicate Glass from the BPRA

The following radionuclides were measured in the borosilicate glass by instrumental gamma-ray spectrometry: ^{22}Na, ^{26}Al, ^{60}Co, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, and ^{155}Eu. The ^{26}Al and ^{22}Na were each determined using a triple-coincidence scheme. The ^{26}Al required the coincident detection of two 511 gamma rays and the 1809 keV line, and the ^{22}Na required the detection of two 511 gamma rays and the 1274 kev line.

Radiochemical separations were performed for ^{238}Pu, $^{239/240}$Pu, ^{241}Pu, ^{241}Am, and ^{244}Cm in the borosilicate glass. These procedures are described in Appendix A.

4.3.3 Analysis of the Boron Carbide from the CRB

The following isotopes were measured in the boron carbide by instrumental gamma-ray spectrometry: ^{22}Na, ^{26}Al, ^{60}Co, ^{137}Cs, ^{152}Eu, ^{154}Eu, and ^{155}Eu. The ^{22}Na and the ^{26}Al were measured using the triple-coincidence system described above for the borosilicate glass. Radiochemical separations were performed for ^{94}Nb, ^{238}Pu, $^{239/240}$ Pu, ^{241}Pu, ^{241}Am, and ^{244}Cm in the boron carbide. These procedures are described in Appendix A.

4.4 Radioanalytical Results from Three Spent Control Rods

The radiochemical concentration data determined in the metal samples from the three control rods are listed in Tables 4.1, 4.2 and 4.3. Tables 4.4 and 4.5 list the radiochemical data observed in the boron carbide from the CRB and the borosilicate glass from the BPRA. All the data have been decay corrected to June 1, 1993.

The following 10 CFR 61 radionuclides were determined in the Type 304 stainless steel metal samples from the CRB: ^{59}Ni, ^{63}Ni, ^{60}Co, and ^{94}Nb. In addition, other long-lived radionuclides, such as ^{54}Mn, ^{93m}Nb, and ^{93}Mo were determined. Cobalt-60 was the most abundant radionuclide, followed by ^{63}Ni which was present at about 10% of the ^{60}Co concentration. The ^{60}Co overwhelmingly contributed to the gamma dose from this assembly since ^{63}Ni is a low energy pure beta emitter. The ^{59}Ni was always present at about 1% of the ^{63}Ni concentration. Niobium-93m (13.8 year half-life) was the third most abundant long-lived radionuclide, being about 300-fold lower then the ^{60}Co concentrations. This radionuclide is produced primarily by the ^{93}Nb (n,n') ^{93m}Nb reaction and to a lesser extent from the decay of ^{93}Mo. The ^{93}Mo (3500 years half-life) is produced in relatively low concentrations by neutron activation of stable Mo present in the stainless steel at a concentration of about 2000 ppm. No long-lived fission products were present in the steel components of the CRB, but trace quantities of fission products and TRU isotopes were observed in the boron carbide material. The radionuclide concentrations in the stainless steel and boron carbide decreased about 20 to 30-fold from the insertion ("hot") end of the assembly to the tail end. The gamma dose rate at the insertion end of the CRB peaked at about 2900R/h at contact in August, 1990, approximately 15 years after removal from service.

Table 4.1 Radionuclide Concentrations Observed in Cruciform Control Rod Blade Samples

Concentration in pCi/g*

Sample ID	Mn-54	Co-60	Ni-59	Ni-63	Nb-93m	Nb-94	Mo-93
DER-1A	4.22E+07	1.10E+10	1.01E+07	9.92E+08	3.02E+07		1.12E+04
DER-1B	5.59E+07	1.32E+10	1.03E+07	9.95E+08	4.56E+07		1.46E+04
DER-1C	4.80E+07	9.36E+09	9.55E+06	9.01E+08	9.41E+07	7.74E+05	9.93E+03
DER-1D	2.56E+07	8.40E+09	9.01E+06	8.68E+08	2.65E+07		1.06E+04
DER-1E	4.29E+07	1.46E+10	1.47E+07	1.48E+09	3.14E+07		2.83E+04
AVG DER-1	4.29E+07	1.13E+10	1.07E+07	1.05E+09	4.56E+07		1.49E+04
±	1.11E+07	2.59E+09	2.27E+06	2.48E+08	2.81E+07		7.69E+03
DER-1Z Cladding**	3.91E+07	8.74E+09	1.27E+07	1.20E+09	7.32E+07		8.46E+03
DER-2B	2.67E+07	6.08E+09	5.57E+06	5.19E+08	1.37E+06		2.11E+03
DER-2C	2.65E+07	7.66E+09	6.50E+06	6.29E+08	1.26E+06	7.71E+04	3.77E+03
DER-2D	3.00E+07	9.70E+09	8.17E+06	7.33E+08	1.28E+06		3.02E+03
DER-2E	2.52E+07	9.38E+09	1.05E+07	9.71E+08	1.38E+06		2.19E+03
AVG DER-2	2.71E+07	8.21E+09	7.69E+06	7.13E+08	1.32E+06		2.77E+03
±	2.04E+06	1.68E+09	2.16E+06	1.93E+08	6.13E+04		7.82E+02
DER-2Z Cladding**	3.01E+07	5.00E+09	7.79E+06	7.92E+08	3.17E+06		5.40E+03
DER-3A	<1.5E+06	1.81E+08	2.32E+05	2.08E+07	1.70E+04		<5.8E+02
DER-3B	<2.8E+06	2.11E+08	2.77E+05	2.78E+07	2.61E+04		<6.4E+02
DER-3C	<1.2E+07	2.23E+08	3.07E+05	2.99E+07	2.57E+04	1.15E+03	<4.1E+02
DER-3D	<8.8E+06	1.61E+08	2.90E+05	2.55E+07	5.62E+04		<2.9E+02
DER-3E	<1.9E+06	2.26E+08	2.28E+05	2.28E+07	2.23E+04		<2.8E+02
DER-3F	<2.9E+06	2.70E+08	3.75E+05	3.63E+07	2.90E+04		<3.2E+02
AVG DER-3	<5.0E+06	2.12E+08	2.85E+05	2.72E+07	2.94E+04		<4.2E+02
±		3.81E+07	5.43E+04	5.54E+06	1.38E+04		
DER-3Z Cladding**	<1.4E+06	1.19E+08	3.49E+05	2.66E+07	4.74E+04		<3.6E+02

*Activity as of June 1, 1993

**The Z-cladding samples were pieces of the outer stainless steel cladding which covered the interior stainless steel tubes (samples A through F) which contained the B_4C neutron poison material (see Figure 4.2).

Table 4.1 Radionuclide Concentrations Observed in Cruciform Control Rod Blade Samples (Cont'd)

Concentration in pCi/g*

Sample ID	Sb-125	Cs-134	Cs-137	Eu-152	Eu-154	Eu-155
DER-1A	<6.8E+07	<7.0E+07	<1.2E+07	<7.2E+07	<8.7E+07	<1.1E+07
DER-1B	<8.0E+07	<8.1E+07	<1.4E+07	<8.5E+07	<1.0E+08	<1.5E+07
DER-1C	<4.7E+07	<4.8E+07	<8.2E+06	<4.9E+07	<6.0E+07	<8.9E+06
DER-1D	<5.5E+07	<5.6E+07	<9.6E+06	<5.7E+07	<7.0E+07	<9.2E+06
DER-1E	<9.7E+07	<9.9E+07	<1.7E+07	<9.9E+07	<1.2E+08	<1.6E+07
AVG DER-1	<6.9E+07	<7.1E+07	<1.2E+07	<7.2E+07	<8.7E+07	<1.2E+07
±						
DER-1Z Cladding**	<7.0E+07	<7.1E+07	<1.2E+07	<6.9E+07	<8.7E+07	<1.2E+07
DER-2B	<5.1E+07	<5.3E+07	<8.9E+06	<5.1E+07	<6.5E+07	<8.6E+06
DER-2C	<5.0E+07	<5.3E+07	<8.8E+06	<5.1E+07	<6.5E+07	<8.5E+06
DER-2D	<6.2E+07	<6.3E+07	<1.1E+07	<6.5E+07	<8.0E+07	<1.0E+07
DER-2E	<4.1E+07	<4.1E+07	<7.2E+06	<4.7E+07	<5.3E+07	<7.7E+06
AVG DER-2	<5.1E+07	<5.2E+07	<9.0E+06	<5.4E+07	<6.6E+07	<8.7E+06
±						
DER-2Z Cladding**	<4.6E+07	<8.1E+06	<4.7E+07	<4.7E+07	<5.9E+07	<7.7E+06
DER-3A	<5.8E+06	<6.0E+06	<1.0E+06	<6.4E+06	<6.4E+06	<1.0E+06
DER-3B	<1.0E+07	<9.2E+06	<1.8E+06	<1.5E+07	<9.7E+06	<1.8E+06
DER-3C						
DER-3D	<3.4E+07	<2.5E+07	<5.8E+06	<5.6E+07	<4.2E+07	<6.0E+06
DER-3E	<7.7E+06	<8.3E+06	<1.2E+06	<7.3E+06	<8.2E+06	<1.3E+06
DER-3F	<1.1E+07	<1.1E+07	<1.8E+06	<1.2E+07	<1.1E+07	<2.0E+06
AVG DER-3	<1.4E+07	<1.2E+07	<2.3E+06	<1.9E+07	<1.6E+07	<2.4E+06
±						
DER-3Z Cladding**	<5.7E+06	<5.5E+06	<9.3E+05	<7.0E+06	<5.2E+06	<1.1E+06

*Activity as of June 1, 1993

**The Z-cladding samples were pieces of the outer stainless steel cladding which covered the interior stainless steel tubes (samples A through F) which contained the B_4C neutron poison material (see Figure 4.2).

Table 4.2 Radionuclide Concentrations Observed in Burnable Poison Rod Assembly (BPRA)

Concentration in pCi/g*

Sample ID	Mn-54	Co-60	Ni-59	Ni-63	Nb-93m	Nb-94	Mo-93
DER-4 outer**	<1.3E+07	2.83E+09	2.22E+07	2.32E+09	1.35E+06	1.63E+04	5.17E+03
DER-4 inner***	<1.6E+06	3.48E+08	1.88E+07	1.91E+09	3.00E+06	4.51E+04	1.92E+04
DER-5 outer	<4.2E+06	3.47E+09	2.46E+07	2.69E+09	1.67E+06		7.42E+03
DER-5 inner	<1.4E+06	4.26E+08	2.20E+07	2.22E+09	3.66E+06		1.22E+04
DER-6 outer	<3.5E+06	3.29E+09	2.49E+07	2.75E+09	1.66E+06		2.53E+03
DER-6 inner	<1.0E+06	3.88E+08	1.99E+07	2.10E+09	3.31E+06		9.89E+03

Sample ID	Sb-125	Cs-134	Cs-137	Eu-152	Eu-154	Eu-155
DER-4 outer	<6.4E+07	<5.8E+07	<9.9E+06	<2.5E+07	<5.3E+07	<1.8E+07
DER-4 inner	<8.5E+06	<1.3E+06	<1.3E+06	<3.6E+06	<6.4E+06	5.03E+06
DER-5 outer	<2.2E+07	<2.0E+07	<3.5E+06	<7.9E+06	<2.3E+07	5.03E+07
DER-5 inner	<7.4E+06	<6.1E+06	<1.2E+06	<2.1E+06	<6.5E+06	<2.1E+06
DER-6 outer	<1.8E+07	<1.7E+07	<2.9E+06	<7.4E+06	<2.0E+07	5.40E+06
DER-6 inner	<5.5E+06	<4.6E+06	<8.7E+05	<1.3E+06	<5.1E+06	4.98E+06

* Activity as of June 1, 1993

** - Samples of the outer stainless steel tube which served as the outer cladding of the borosilicate glass poison tube

***- Samples of the inner stainless steel tube which served as the inner cladding of the borosilicate glass poison tube

Table 4.3 Radionuclide Concentrations Observed in Reactor Rod Cluster Control Assembly (RCCA) Samples

Concentration in pCi/g (as of 6/1/93)

Type 304 Stainless Steel Cladding Samples , Ag-In-Cd Alloy, and Stainless SteelControl Rod Tip (RCCA-8 ss)

Sample ID	Na-22	Al-26	Mn-54	Co-60	Ni-59	Ni-63	Nb-93m	Nb-94	Mo-93	Ag-108m
DER-7 ss			<14	1.22E+03	<26	5.87E+02				---
DER-7 Ag-In-Cd				3.79E+02						5.44E+03
DER-8 ss			<62	2.67E+03	<22	1.43E+03				---
DER-8 Ag-In-Cd				9.71E+02						1.12E+04
DER-9 ss			2.18E+02	3.33E+05	2.69E+03	2.46E+05				---
DER-9 Ag-In-Cd	<4	<4		7.09E+03						1.11E+06
DER-10 A ss			1.1E+07	2.99E+10	2.87E+07	2.93E+09	3.60E+07	5.44E+05	2.07E+04	---
DER-10 A Ag-In-Cd	<2.2E+04	<1.4E+04	3.1E+07	1.68E+09	4.70E+02	6.31E+04	8.08E+04			2.14E+10
DER-10 B ss			1.1E+08	3.75E+10	4.16E+07	4.15E+09	2.09E+07		2.31E+04	8.92E+07
DER-10 B Ag-In-Cd			4.4E+07	2.97E+09	1.70E+03	1.01E+05			<1.3E+02	2.73E+10
RCCA -8 ss*			1.11E+07	6.49E+09	[illegible]8E+07	8.24E+09	1.19E+06		1.44E+04	

Sample ID	Ag-110m	Cd-109	Cd-113m	Sb-125	Cs-134	Cs-137	Eu-152	Eu-154	Eu-155
DER-7 ss					<74	<13	<110	<94	<22
DER-7 Ag-In-Cd	1.55E+02				<40	<7	<36	<180	<12
DER-8 ss				214	<2.7E+02	<56	<6.0E+02	<3.5E+02	<81
DER-8 Ag-In-Cd	3.82E+02				<53	<9	<43	370	<15
DER-9 ss				<2.7E+03	<2.8E+03	<4.6E+02	<2.6E+03	<3.3E+03	460
DER-9 Ag-In-Cd	3.96E+04	8.59E+03	5.15E+05		<3.6E+02	<65	<1.9E+02	3240	215
DER-10 A ss				<4.4E+07	<4.8E+07	<7.2E+06	<4.0E+07	<5.3E+07	<7.3E+06
DER-10 A Ag-In-Cd	1.48E+09	6.85E+06	4.93E+08	<2.9E+08	<2.0E+08	<3.4E+07	<1.2E+08	<8.7E+08	<6.5E+07
DER-10 B ss				<4.2E+08	<4.5E+08	<6.8E+07	<3.8E+08	<4.9E+08	<6.9E+07
DER-10 B Ag-In-Cd	2.32E+09	1.42E+07	8.68E+08	<4.0E+08	<3.0E+08	<4.9E+07	<1.8E+08	<1.4E+09	<8.7E+07
RCCA -8 ss				<5.9E+07	<5.2E+07	<9.4E+06	<1.5E+07	<6.0E+07	1.01e+08

*A sample of RCCA-8, the stainless steel tip end of the insertion end of RCCA was sampled by Migliori, et al., 1994 and shared with us for radiochemical analyses and comparison of results.

Table 4.4 Radionuclide Concentrations in Boron Carbide Material from Cruciform Control Rod Blade (CRB) Samples

Concentration in pCi/g (as of 6/1/93)

Sample ID	Na-22	Al-26	Mn-54	Co-60	Nb-94	Sb-125	Cs-134	Cs-137
DER-1	<1.6E+04		1.87E+05	1.06E+07	<2.6E+04	<1.4E+05	<1.4E+05	8.69E+04
DER-2	<49	<92	1.86E+05	5.71E+06	<1.3E+04	<7.0E+04	<7.1E+04	2.67E+04
DER-3	<41	<84	<5.4E+03	5.68E+05	<3.6E+03	<2.2E+04	<1.5E+04	1.99E+05

Sample ID	Eu-152	Eu-154	Eu-155	Pu-238	Pu-39/240	Pu-241	Am-241	Cm-244
DER-1	4.09E+04	8.56E+04	<6.3E+04	1.64E+04	6.34E+03	4.65E+05	6.80E+03	1.25E+04
DER-2	4.50E+04	4.82E+04	<3.1E+04					
DER-3	<1.7E+04	<1.6E+04	<8.0E+04					

Table 4.5 Radionuclide Concentrations Observed in Borosilicate Glass Specimens from the Burnable Poison Rod Assembly (BPRA) Samples

Concentration in pCi/g (as of 6/1/93)

Sample ID	Na-22	Al-26	Mn-54	Co-60	Sb-125	Ba-133	Cs-134	Cs-137
DER-4	4.85E+02	<4.1	<1.8E+03	9.96E+05	4.96E+03	1.55E+04	6.60E+03	2.17E+04
DER-5	5.85E+02	<6.6	<1.9E+03	1.15E+06	7.35E+03	1.38E+04	6.96E+03	2.76E+04
DER-6	6.89E+02	<5.2	<1.4E+03	1.01E+06	6.79E+03	1.29E+04	7.49E+03	2.40E+04

Sample ID	Eu-152	Eu-154	Eu-155	Pu-238	Pu-239/240	Pu-241	Am-241	Cm-244
DER-4	2.03E+04	4.62E+05	1.47E+05					
DER-5	8.15E+03	4.80E+05	1.49E+05					
DER-6	1.67E+04	4.74E+05	1.52E+05	1.02E+02	5.73E+02	6.51E+04	2.55E+03	1.08E+02

The boron carbide from the BWR control rod was dominated by ^{60}Co, but also observed by instrumental analysis was ^{137}Cs, ^{152}Eu, and ^{154}Eu. Radiochemical determinations also showed the presence of ^{238}Pu, $^{239/240}Pu$, ^{241}Pu, ^{241}Am, and ^{244}Cm.

The Ag-In-Cd control rod was unique in its elemental makeup, and consequently, the presence of ^{108m}Ag, ^{110m}Ag, ^{109}Cd, and ^{113m}Cd was also determined. Indium does not produce any long-lived neutron activation product radioisotopes. It is important to note that the activity of ^{108m}Ag was as great or greater than the activity of ^{60}Co. Silver-108m, with a half-life of 130 years, will be the most abundant radionuclide in this type of control rod (RCCA) for hundreds of years, and will need to be considered in the disposal of these types of control rods. Silver-108 decays mainly by electron capture accompied by the emission of three relatively high energy gamma rays (439, 614, and 722 keV) each at 91% relative intensity, and therefore has a relatively high gamma dose conversion factor. On a per gram basis, the concentration of ^{108m}Ag in this alloy is comparable to the ^{60}Co concentrations in the stainless steel cladding, but the mass of the Ag/In/Cd alloy greatly exceeds that of the stainless steel cladding. Therefore, the ^{108m}Ag will be the dominant gamma dose-contributing radionuclide in this type of control rod assembly for many hundreds of years. Silver-108m is not addressed in 10CFR61, so it cannot be considered in waste classification assessments for this assembly.

The RCCA was fully withdrawn at all times during full power operations and only the first few tens of cm on the insertion end of the RCCA were highly neutron activated. The gamma dose rate at the insertion end peaked at about 290 R/h at contact in August 1990.

The Ag-In-Cd alloy in the RCCA also contained two long-lived Cd neutron activation products, ^{109}Cd (453 days half-life) and ^{113m}Cd (13.7 years half-life). The ^{113m}Cd, because of its greater abundance and longer half-life is the more important from waste disposal considerations. The ^{113m}Cd decays by emission of a medium energy (590 keV) beta particle and a very low relative intensity 264 keV gamma ray from a 0.1% isomeric transistion. The ^{113m}Cd concentrations in the neutron poison alloy of the CRB were about 30-fold lower than the ^{108m}Ag concentrations.

The PWR Burnable Poison Rod Assembly, composed of stainless steel clad borosilicate glass, likewise contained predominantly ^{60}Co produced from 1600 ppm of cobalt present in the steel. This steel likewise contained similar amounts of ^{63}Ni, ^{93m}Nb, ^{59}Ni, and ^{94}Nb, relative to the ^{60}Co, as observed in the CRB. The concentrations of the activation products were rather uniformly distributed over the length of the neutron-absorbing section of the BPRA. The gamma dose rate over this section was about 120 R/h at contact in August, 1990. The borosilicate glass found in the BPRA was dominated by ^{60}Co activity, and the radioisotopes ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, and ^{155}Eu were also determined instrumentally. In addition, ^{238}Pu, $^{239/240}Pu$, ^{241}Am and ^{244}Cm were determined by radiochemical methods. These would appear to be present as the result of uranium impurities in the glass. All of the radionuclides in the glass contributed insignificantly to the waste classification of the BPRA.

4.5 Stable Element Analysis by ICP/MS

Knowledge of the chemical composition of the various components found in the control rod assemblies is necessary if one wants to predict the neutron activation products present after some period of neutron exposure. Therefore, dissolved aliquots of the metal specimens from the control rods, dissolved aliquots of the boron carbide collected from the CRB samples, and dissolved aliquots of the borosilicate glass were analyzed for their major, minor, and trace elements. Because these materials had already been irradiated, it was not a simple task to determine the chemical composition because of the requirement to handle high-dose rate materials. At PNL, an inductively coupled plasma/mass spectrometer (ICP/MS) has been modified to accommodate radioactive materials for multi-element analyses (Wyse 1993). Representative samples of the type 304 stainless steel obtained from the cladding of the control rods were chosen as well as an aliquot from each CRB sample that contained boron carbide and each BPRA that contained the borosilicate glass. Of concern, was the possibility of burnup of some of the elements that might alter the analytical results. This depletion would vary with each control rod and each sample because of the varying neutron exposure both due to time of exposure and location relative to the reactor core.

Briefly, the ICP/MS is operated by taking a liquid aliquot and aspirating it through a pneumatic nebulizer which mixes it with argon to form an aerosol. The aerosol is injected into the inductively coupled plasma where the plasma atomizes and ionizes the aerosol. This ion beam is then focused and sent through a quadrapole mass spectrometer which separates the ions according to mass per unit charge (m/z). Ions are detected with an electron multiplier and by varying the radio frequency/magnetic fields of the quadrapole, the masses of interest can be scanned. The concentration results are obtained by ratioing count rates for known isotopic ratios to the count rates obtained for the unknown samples. Therefore, it is very

important that the ICP/MS analyst not choose an isotope for the standard that becomes depleted after neutron exposure in the reactor core. Also, one wants the quantity of a element at the beginning of exposure, not at some later time because that is what is needed for predictive modeling.

The major, minor, and trace elements that were measured in the type 304 stainless steel samples from each assembly and the Ag-In-Cd absorber in the RCCA samples are listed in Table 4.6. Evans, et al. (1984) reported a composition summary of Type 304 stainless steel samples obtained from a number of commercial reactors. The reported average concentrations for Cr, Mn, Fe, Ni, and Mo were 18.4 ± 1.1%, 1.53 ± 0.28%, 70.6 ± 2.6%, 10.0 ± 0.7%, and 0.26 ± 0.15%, respectively. Table 4.6 shows considerable variability in the concentrations observed for Cr, Mn, Fe, Ni, and Mo from one set of control rod samples to another.

4.5.1 Type 304 Stainless Steel Samples from the CRB, BPRA, and RCCA

The measured concentration results for the type 304 stainless steel samples obtained from the three control rods are listed in Table 4.6. There appears to be reasonable agreement with the data reported by Evans et al. (1988) for 304 stainless steel compared to that of the CRB although it appears that the concentrations of Fe and Ni in the CRB are slightly higher. The mass balance appears reasonable. The BPRA samples appear to have a higher concentration of Cr and Ni compared to the data reported by Evans et al. (1988), thus resulting in mass balances of 112 and 130. The fact that the concentration of Fe in the DER-6 outer sample is less than that of the DER-6 inner is consistent with the theory that the outer tube was exposed to a higher neutron flux compared to the inner tube because of the borosilicate glass (neutron poison) tube between the inner and outer stainless steel tubes. The RCCA samples were high in Cr and Fe compared to the ranges reported by Evans et al., (1988). In fact, the mass balances for these two samples were 121 and 134%.

4.5.2 Ag-In-Cd Metal Sample from the RCCA

The composition of the absorber used in the RCCA has been reported to be 80% Ag, 15% In, and 5% Cd. Table 4.6 lists the major, minor, and trace elements found in the Ag-In-Cd rod. The measured results were 93% and 83% Ag in samples from DER-7 and -9. The measured In was 16% for both samples and the measured Cd was about 5.4%. The mass balances were 114.5% and 105.5%, respectively.

4.5.3 Boron Carbide from the Control Rod Blade (CRB) Samples

The measured data for the boron carbide is listed in Table 4.7. It was not possible to measure the C content in these samples since the C analyzer had been removed from the hot cell. The concentration of B was not determined. However, there were small amounts of Al, Mn, Co, and Ba measured in the B_4C. Of these, the most abundant was Co, being present at about 3%.

4.5.4 Borosilicate Glass from the Burnable Poison Rod Assembly (BPRA) Samples

Some of the major, minor, and trace elements found in the borosilicate glass are reported in Table 4.7. The four dominant elements measured were Al, Na, B, and Li. The neutron absorbing elements were the B and Li.

In addition, ^{10}B and ^{11}B were measured in the glass samples to obtain their isotopic ratios. It has been suggested that the ratio $^{10}B/^{11}B$ would be a good indicator of the neutron fluence that the highly irradiated metals were exposed to. The ratio of $^{10}B/^{11}B$ would be an indicator of the thermal neutron exposure. The isotopic ratio ($^{10}B/^{11}B$) for normally abundant ^{10}B and ^{11}B is 0.248. In samples of the glass for DER-4, DER-5, and DER-6, the $^{10}B/^{11}B$ ratios were measured to be 0.014 ± 0.002, 0.007 ± 0.001, and 0.011 ± 0.002, respectively, indicating substantial burnup.

4.6 Comparison to Other Reported Radioanalytical Measurements

As mentioned in the introduction, this program was related to a DOE-sponsored program that was designed to measure a limited number of nuclides in the control rod specimens. The DOE data are reported in a document titled "Non-Fuel Assembly Components: 10 CFR 61.55 Classification for Waste Disposal" by R. J. Migliore, et al. (1994). Migliore et al. reported concentration data for only six radionuclides (^{14}C, ^{60}Co, ^{59}Ni, ^{63}Ni, ^{94}Nb, and ^{99}Tc) and only for the stainless steel cladding on each assembly. Table 4.8 lists their data along with our data for comparison of analytical results. This work has determined four of the nuclides that were also determined by Migliore et al. (1994).

Table 4.6 Major, Minor, and Trace Elements Determined in Metal Samples

Concentration in ug/g

Sample ID	Cr	Mn	Fe	Co	Ni	Cu	Zn	Zr
Cruciform Control Rod Blade (CRB) - Stainless Steel								
DER-1E	1.51E+05	7.37E+03	5.93E+05	2.95E+03	9.79E+04	4.10E+03	1.64E+03	2.90E+03
±						1.52E+03	1.21E+03	
DER-3D	2.19E+05	2.05E+04	7.71E+05	2.87E+03	1.18E+05	4.23E+03	2.03E+03	4.25E+03
±							4.36E+02	1.58E+03
DER-3D (Dup)	2.12E+05	1.76E+04	7.71E+05	2.46E+03	1.14E+05	4.17E+03	5.50E+02	4.97E+02
±							5.38E+02	
DER-3E	2.00E+05	9.42E+03	7.43E+05	3.70E+03	1.14E+05	4.57E+03	7.67E+02	5.27E+02
±							4.56E+02	
DER-3Z	1.91E+05	2.10E+04	7.10E+05	2.27E+03	1.13E+05	3.51E+03	3.12E+03	1.51E+03
±			9.68E+04					5.56E+02
Burnable Poison Rod Assembly (BPRA) - Stainless Steel								
DER-4 outer	2.65E+05	1.92E+04	7.03E+05	1.31E+03	1.26E+05	1.16E+03	7.56E+02	1.62E+02
±								
DER-6 outer	2.42E+05	2.11E+04	7.09E+05	1.61E+03	1.38E+05	1.15E+03	<9.96E+00	3.98E+01
±								1.39E+01
DER-6 inner	2.27E+05	1.91E+04	7.85E+05	1.90E+03	1.57E+05	2.13E+03	1.94E+03	2.86E+02
Reactor Rod Cluster Control Assembly (RCCA) - Stainless Steel (ss) and Ag-In-Cd Alloy (Ag)								
DER-7 ss	2.83E+05	2.07E+04	7.53E+05	8.47E+02	1.45E+05	1.36E+03	<9.92E+00	3.89E+01
±								
DER-9 ss	3.35E+05	2.00E+04	8.01E+05	6.02E+02	1.47E+05	1.56E+03	1.30E+03	1.19E+02
±								4.28E+01
DER-7 Ag	<1.55E+00	<1.55E+00	<1.55E+01	6.13E+01	7.54E+02	8.04E+02	3.79E+02	7.00E+00
±								
DER-9 Ag	<2.16E+00	<2.16E+00	<2.16E+01	6.86E+01	9.32E+02	9.19E+02	4.60E+02	1.29E+01
±								4.96E+00
DER-9 Ag (Dup)	<2.16E+00	<2.16E+00	<2.16E+01	6.82E+01	1.20E+03	8.72E+02	3.84E+02	9.49E+00
±								3.88E+00

Table 4.6 Major, Minor, and Trace Elements Determined in Metal Samples (Cont'd)

Concentration in ug/g

Sample ID	Nb	Mo	Ag	Cd	In	Sn	Sb	Pb
Cruciform Control Rod Blade (CRB)								
DER-1E	<1.01E+02	8.83E+02	<1.01E+02			1.11E+02	<1.01E+02	2.20E+03
±						8.04E+01		1.08E+03
DER-3D	<5.98E+01	1.79E+03	<5.98E+01			8.73E+01	<5.98E+01	6.34E+02
±								3.71E+02
DER-3D (Dup)	<5.98E+01	1.71E+03	<5.98E+01			9.80E+01	<5.98E+01	3.47E+02
±								1.14E+02
DER-3E	<5.85E+01	2.22E+03	<5.85E+01			4.68E+01	<5.85E+01	2.20E+04
±						2.11E+02		7.84E+03
DER-3Z	<8.06E+01	2.65E+03	<8.06E+01			<8.06E+01	<8.06E+01	5.32E+02
±								8.39E+02
Burnable Poison Rod Assembly (BPRA)								
DER-4 outer	<1.34E+01	9.20E+02	<1.34E+01			8.86E+01	<1.34E+01	6.43E+01
±								2.33E+02
DER-6 outer	<9.96E+00	1.20E+03	1.07E+04			1.29E+01	<9.96E+00	<9.96E+00
±			5.98E+03			6.08E+01		
DER-6 inner	<7.55E+01	1.77E+03	1.00E+05			2.79E+02	<7.55E+01	<7.55E+01
						1.13E+02		
Reactor Rod Cluster Control Assembly (RCCA)								
DER-7 ss	<9.92E+00	2.67E+03	6.40E+03			7.12E+01	<9.92E+00	1.59E+01
±			1.98E+03					7.24E+01
DER-9 ss	<1.53E+01	2.42E+03	2.95E+04			1.06E+02	<1.53E+01	1.83E+02
±			9.79E+03			3.36E+01		8.56E+01
DER-7 Ag	<1.55E+00	1.55E+00	9.28E+05	5.30E+04	1.62E+05	2.07E+01	<1.55E+00	4.56E+01
±		4.04E+00						
DER-9 Ag	<2.16E+00	2.07E+01	8.37E+05	5.35E+04	1.62E+05	1.60E+01	<2.16E+00	2.33E+01
±		9.71E+00				5.18E+00		
DER-9 Ag (Dup)	<2.16E+00	<2.16E+01	8.20E+05	5.67E+04	1.64E+05	1.56E+01	<2.16E+00	3.97E+01

Table 4.7 Selected Major, Minor, and Trace Elements in Boron Carbide and Borosilicate Glass Samples

Concentration in ug/g

Sample ID	Li	Be	B	Na	Al	Mn	Co	Ba	Eu	Sm
Cruciform Control Rod Blade (CRB) - Boron Carbide										
DER-1BC					7.27E+02	7.13E+00	3.02E+04	7.29E+00	<1	<1
					1.85E+02	5.96E+00		5.03E+00	<1	<1
DER-2BC										
					1.15E+03	6.06E+01	2.98E+04	1.70E+01	<1	1.5
DER-3BC										
Burnable Poison Rod Assembly (BPRA) - Borosilicate Glass										
DER-4G	7.57E+03	<1	3.83E+04	3.28E+04	1.60E+04	4.26E+00	<1	1.31E+01	<1	<1
±	1.08E+03					9.57E-01				
DER-5G	9.20E+03	2.53E+00	4.72E+04	2.15E+04	3.81E+04	1.11E+01	1.20E+00	1.63E+01	<1	<1
±		1.04E+00					4.00E-01			
DER-6G										
	1.15E+04	9.22E+00	3.52E+04	1.62E+04	3.49E+04	0.00E+00	<1	2.11E+01	<1	<1
±		1.50E+01								

Table 4.8 Comparison of Our Data to Reported Data* for the Metal Cladding on the Control Rod Assemblies

Activity in Ci/g

Sample ID			^{60}Co		^{59}Ni		^{63}Ni		^{94}Nb	
this work	Migliore		this work	Migliore	this work	Migliore	this work	Migliore	this work	Migliore
Control Rod Blade (CRB)										
DER-1	CRB-3	z**	8.74E-03	1.02E-02	1.27E-0	1.28E-05	1.20E-03	1.59E-03	7.74E-07	2.81E-08
		a	1.10E-02		1.01E-05		9.92E-04			
		b	1.32E-02		1.03E-05		9.95E-04			
		c	9.36E-03		9.55E-06		9.01E-04			
		d	8.40E-03		9.01E-06		8.68E-04			
		e	1.46E-02		1.47E-05		1.48E-03			
		avg	1.13E-02		1.07E-05		1.05E-03			
DER-2	CRB-6	z	5.00E-03	5.55E-03	7.79E-06	8.09E-06	7.92E-04	9.76E-04	7.71E-08	1.09E-08
						7.76E-06		9.74E-04		
		b	6.08E-03		5.57E-06		5.19E-04			
		c	7.66E-03		6.50E-06		6.29E-04			
		d	9.70E-03		8.17E-06		7.33E-04			
		e	9.38E-03		1.05E-05		9.71E-04			
		avg	8.21E-03		7.69E-06		7.13E-04			
DER-3	CRB-9	z	1.19E-04	1.45E-04	3.49E-07	1.97E-07	2.66E-05	2.64E-05	1.15E-09	1.29E-10
						2.90E-07		3.90E-05		
		a	1.81E-04		2.32E-07		2.08E-05			
		b	2.11E-04		2.77E-07		2.78E-05			
		c	2.23E-04		3.07E-07		2.99E-05			
		d	1.61E-04		2.90E-07		2.55E-05			
		e	2.26E-04		2.28E-07		2.28E-05			
		f	2.70E-04		3.75E-07		3.63E-05			
		avg	2.12E-04		2.85E-07		2.72E-05			
Burnable Poison Rod Assembly (BPRA)										
DER-4 outer	BPRA-6		2.83E-03	2.99E-03	2.22E-05	2.61E-05	2.32E-03	2.93E-03	1.63E-08	1.13E-08
DER-4 inner			3.48E-04		1.88E-05		1.91E-03			
DER-5 outer			3.47E-03		2.46E-05		2.69E-03			
DER-5 inner			4.26E-04		2.20E-05		2.22E-03			
DER-6 outer			3.29E-03		2.49E-05		2.75E-03			
DER-6 inner			3.88E-04		1.99E-05		2.10E-03			
Rod Cluster Control Assembly (RCCA)										
DER-7	RCCA-3		1.22E-09	6.35E-07	<2.60E-11	8.75E-10	5.87E-10	1.07E-07		
DER-8	RCCA-5		2.67E-09	1.97E-07	<2.20E-11	3.15E-10	1.43E-09	4.81E-08		
DER-9	RCCA-7		3.33E-07		2.69E-09		2.46E-07			
DER-10A			2.99E-02		2.87E-05		2.93E-03		5.44E-7	7.83E-9
DER-10B			3.75E-02		4.16E-05		4.15E-03			
RCCA-8	RCCA-8		6.49E-03	6.49E-03	7.18E-05	8.24E-05	8.24E-03	1.02E-02		
						7.95E-05		9.76E-03		

*Reported data is that of Migliore et al., 1994.

**"z" stands for metal cladding which is what Migliore et al analyzed. Samples a-f are the stainless steel tubes that were contained within the metal cladding.

In general there was excellent agreement between the results we reported and those reported by Migliore et al. (1994), with agreement being in the range of 1% to 25%, except for ^{94}Nb where our overall results average about 23 times higher. For example, the control rod blade activity data show excellent agreement between the two sets of results, except for the ^{94}Nb where our results averaged about 14 times higher. Migliore et al. (1994), only analyzed the cladding that surrounded the stainless steel tubes that were within the CRB, and this corresponds to sample "z" that we reported. In addition, we also have data for a number of stainless steel tubes that were within the CRB and these are samples labeled "a" through "f" (four to six tubes were sampled). These data are also presented in Table 4.8.

There was only one sample for comparison of results for the BPRA. Our sample DER-5-outer corresponds to the reported data for sample BPRA-6. Again, there is excellent agreement for all radionuclides, including ^{94}Nb.

However, there was disagreement in the values observed in the RCCA specimens sampled from the low activity end of the rod. It is believed that this difference was due to the fact that we took great care in conducting numerous decontaminating and cleaning steps for our samples prior to analysis, while it appears that there was still some fission and activation product contamination derived from the hot cell environment where the samples were prepared. For the one sample with high activity (RCCA-8), there was excellent agreement between the results, but at the low activity end of the RCCA our ^{60}Co and ^{63}Ni values were 200 to 500 times lower than those reported by Migliori, et al. (1994), indicating contamination of their samples.

5 Comparison of Empirical versus Calculated Radionuclide Inventories

5.1 Calculation of Curie Content from Empirical Results

Following the empirical determination of the radionuclides present in the control rods, calculations were performed to determine the total Curie content of each type of control rod assembly.

An example illustrating the calculation of total Curie content for the Control Rod Blade follows. The length of the control rod of interest is 143 in. Each control rod contains 84 tubes with a diameter of 0.138 in and wall thickness of 0.025 in. The density of type 304 stainless steel is 8.0 g/cm^3. The total mass of each rod was calculated to be 240 g or 20.2 kg for the 84 rods in the assembly.

Experimentally, samples were taken from three locations along the length of the CRB. These are noted on the schematic of the CRB (Figure 2.1). If this was the only data available, the CRB would be divided into three segments and the Curie content calculated for each segment based on the measured data. However, it was possible to calculate a finer grid using the data obtained from the TLD measurements taken for the direct assay measurements described in Section 3. It should be noted that this process must be performed for each material found and analyzed in the CRB. Thus, calculations were performed for the stainless steel outer cladding, the inner cylindrical stainless steel tubes containing the boron carbide, and the boron carbide contained within the cylindrical tubes to obtain the total Curie content of the CRB.

The ^{60}Co activity determined for each TLD was tabulated for each location along the control rod. Then the measured activity at the three known locations was ratioed to the corresponding TLD ^{60}Co data and the ^{60}Co activities were interpolated for other TLD measurement locations. A ^{60}Co activity was then obtained for each of the TLD measurement locations along the CRB. Then, assuming that each segment was 20 g, the ^{60}Co activity per segment per tube was calculated. This value was then multiplied by 84 to get the total activity for all of the stainless steel rods and was determined to be 122.9 Ci as of June 1, 1993.

A similar calculation was performed for the stainless steel that acted as a cladding sheath around the cylindrical rods. Documentation of the CRB assembly indicated that it weighed 218 pounds or 98.9 kg. The weight of the B_4C contained within the tubes was calculated to be 5.18 kg (density of B_4C is 1.76 g/cm^3), and the tubes themselves weighed 20.2 kg. Assuming the remaining weight is due to the stainless steel sheath, the weight of the sheath was 73.5 kg.

Again, using the TLD data and our measured activity data, the activity of ^{60}Co was interpolated between the measured locations. Using the process described above, the total ^{60}Co activity was calculated to be 159.5 Ci for the sheath.

A similar calculation was also performed for the B_4C powder that was collected. The activity of ^{60}Co contained in the B_4C within the 84 rods was calculated to be 0.024 Ci.

The total calculated ^{60}Co activity as of June 1, 1993 was 282.4 Ci for the entire Control Rod Blade, excluding the top stellite section and the botttom velocity limiter.

Similar calculations were made for the Burnable Poison Rod Assembly (BPRA) which yielded a ^{60}Co Curie content of 20 Ci. Similar calculations were also made for the reactor Rod Cluster Control Assembly (RCCA). A value of ^{60}Co was calculated but it was also necessary to calculate the activities of ^{110m}Ag and ^{108m}Ag. The assumption was made that the Ag isotopes correlate with the ^{60}Co activity so that the TLD data could be used in the calculations. The calculated concentrations were 7.3 Curies of ^{60}Co, 10.8 Ci of ^{108m}Ag, and 1.1 Ci of ^{110m}Ag as of June 1, 1993.

Table 5.1 shows the Curie content results obtained from our empirical data compared to the Curie contents obtained by the two direct-assay methods. The activity of the BWR CRB and the PWR BPRA was dominated by ^{60}Co. The agreement observed for the BWR CRB between the empirically measured values and the results for the two direct-assay methods is quite good; 282 Curies empirically measured versus 246 Curies (Integral Dose Method) or 187 Curies (MCNP Method) by the direct-assay techniques. The agreement for the PWR BPRA empirical (20 Curies) versus direct-assay measurement (22 Curies for Integral Dose or 23 Curies for the MCNP method) was remarkably good. This good agreement lends confidence to the direct-assay methodology used to nondestructively determine the Curie contents of highly radioactive metal-waste components.

The calculation of the total Curie content of the RCCA was a bit more difficult since the activity was not dominated by just the ^{60}Co, but also significant concentrations of ^{108m}Ag and ^{110m}Ag needed to be calculated. In addition, there was a very sharp gradient in activity at the tip of the control rod as observed in the activity data for sample DER-9 and DER-10 A and B. The total Curie conent of gamma-emitting radionuclides of this control rod as of June 1, 1993

Table 5.1 Comparison of Radionuclide Contents in Spent Control Rods by Direct Assay and Sampling/Analysis Methods (Inventories in Curies)*

Method	BWR Cruciform Control Rod Blade	PWR Burnable Poison Control Rod	PWR Rod Cluster Control Assembly		
	^{60}Co	^{60}Co	^{60}Co	^{108m}Ag	^{110m}Ag
Empirical	282	20	7.3	10.8	1.1
Direct Assay					
---Integral dose	246	22	2.6	10.6	0.4
---MCNP Method	187	23	2.3	9.4	0.4

*Activities decay corrected to June 1, 1993.

calculated from the empirical data, yielded a value of 19.2 Curies (7.3 Ci ^{60}Co, 10. 8 Ci ^{108m}Ag, and 1.1 Ci ^{110m}Ag) versus 13.6 Ci (2.6 Ci ^{60}Co, 10.6 Ci ^{108m}Ag, and 0.4 Ci ^{110m}Ag) for tl rect assay Integral Dose Method, or 12.1 Ci (2.3 Ci 9.4 Ci ^{108m}Ag, and 0.4 Ci ^{110m}Ag) for the direct-assay MCNP Method.

5.2 Comparison of Empirical vs. Calculated Radionuclide Concentrations in Control Rods

The empirically determined Curie content from this work and Migliore et al. (1994) has been tabulated for ^{60}Co, ^{59}Ni, ^{63}Ni, and ^{94}Nb in Tables 5.2, 5.3, 5.4, and 5.5. In addition to the empirical results, the Tables also include the results obtained by Migliore et al. (1994) when using predictive methodologies such as ORIGEN2 and MCNP. Since the dominant radionuclide activities observed in the control rods was from the type 304 stainless steel used for the cladding and tubing of these control rods, the results of Migliore et al. (1994) for the Curie contents are consistent with our results, with one exception. The contribution of the Ag from the Ag-In-Cd absorber needs to be considered when one is calculating the Curie contents of the RCCA. Since ^{108m}Ag has a half-life of 130 years, it will become the dominant dose-contributing radionuclide for hundreds of years in this type of control rod assembly.

Our empirical data in Tables 5.2, 5.3, 5.4, and 5.5 has been converted from activity per gram of metal to activity per cubic meter of metal to enable the comparison to the ORIGEN2 and MCNP results which were reported in Ci/m^3 of metal in Migliore et al. (1994). The conversion factor was the density of type 304 stainless steel, 8.00 g/cm^3. As noted earlier, there was good agreement between our experimental results and that presented by Migliore et al. (1994) for the stainless steel samples. The ORIGEN2 results for the CRB was generally lower than the expermental values except for the bottom 1/4 where the calculated results were higher. The BPRA comparison showed an ORIGEN result that was 1.5-2 times the empirically determined value. The RCCA comparison showed that the ORIGEN2 results were about 4 times lower compared to the empirical measurements.

Our empirical results can be compared to the MCNP results for the BPRA sample 6. The MCNP result was lower than the empirical data by about a factor of 3.5. The empirical results for the RCCA samples were also compared to the MCNP result. The MCNP result was low compared to the laboratory results by a factor of 3.6.

Table 5.2 Comparison of Empirical and Calculated Curie Contents for ^{60}Co

Activity in Ci/m^3

This work		Migliore et al. (1994)					
		Laboratory Results		ORIGEN2 - Calculated		MCNP - Calculated	
Sample ID	Activity	Sample ID	Activity	Sample ID	Activity	Sample ID	Activity
		Control Rod Blade Assembly (CRB)					
DER-1 (z)	7.00E+04	C-3	8.16E+04	CRB Top 1/4	1.95E+04		
DER-2(z)	4.00E+04	C-6	4.44E+04	CRB 3rd 1/4	1.61E+04		
DER-3(z)	9.52E+02	C-9	1.16E+03	CRB Bottom 1/4	5.97E+03		
		C-9 (duplicate)	1.11E+03				
		Burnable Poison Rod Assembly (BPRA)					
DER-5 outer	2.78E+04	BPRA-6	2.39E+04	BPRA-6	4.00E+04	BPRA-6	7.06E+03
		Reactor Rod Cluster Control Assembly (RCCA)					
DER-7 ss	9.76E-03	RCCA-3	5.08E+00	RCCA	5.84E+05		
DER-8 ss	2.14E-02	RCCA-5	1.58E+00				
DER-9 ss	2.66E+00	RCCA-7					
RCCA-8	5.19E+04	RCCA-8	5.19E+04			RCCA-8	1.43E+04

Table 5.3 Comparison of Empirical and Calculated Curie Contents for ^{59}Ni

Activity in Ci/m^3

This work		Migliore et al					
		Laboratory Results		ORIGEN2 - Calculated		MCNP - Calculated	
Sample ID	Activity	Sample ID	Activity	Sample ID	Results	Sample ID	Results
		Control Rod Blade Assembly (CRB)					
DER-1(z)	1.02E+02	C-3	1.02E+02	CRB Top 1/4	1.79E+01		
DER-2(z)	6.23E+01	C-6	6.47E+01	CRB 3rd 1/4	1.35E+01		
		C-6 (duplicate)	6.21E+01				
DER-3(z)	2.79	C-9	1.58E+00	CRB Bottom 1/4	4.08		
		C-9 (duplicate)	2.32E+00				
		Burnable Poison Rod Assembly (BPRA)					
DER-5 outer	1.97E+02	BPRA-6	2.09E+02	BPRA-6	2.51E+02	BPRA-6	2.27E+01
		Reactor Rod Cluster Control Assembly (RCCA)					
DER-7 ss	<2.1E-04	RCCA-3	7.00E-03	RCCA	1.18E+03		
DER-8 ss	<1.8E-04	RCCA-5	2.52E-03				
DER-9 ss	2.15E-02	RCCA-7					
RCCA-8	5.74E+02	RCCA-8	6.59E+02			RCCA-8	4.52E+01

Table 5.4 Comparison of Empirical and Calculated Curie Contents for ^{63}Ni

Activity in Ci/m^3

		Migliore et al					
This work		Laboratory Results		ORIGEN2 - Calculated		MCNP - Calculated	
Sample ID	Activity	Sample ID	Activity	Sample ID	Activity	Sample ID	Activity
		Control Rod Blade Assembly (CRB)					
DER-1 (z)	9.60E+03	C-3	1.27E+04	CRB Top 1/4	2.37E+03		
DER-2 (z)	6.34E+03	C-6	7.81E+03	CRB 3rd 1/4	1.80E+03		
DER-3 (z)	2.13E+02	C-9	7.79E+02	CRB Bottom 1/4	5.84E+02		
		C-9 (duplicate)	2.11E+02				
		Burnable Poison Rod Assembly (BPRA)					
DER-5 outer	BPRA-6	2.34E+04	BPRA-6	2.89E+04	BPRA-6	2.52E+03	
		Reactor Rod Cluster Control Assembly (RCCA)					
DER-7 ss	4.70E-03	RCCA-3	8.56E-01	RCCA	1.91E+05		
DER-8 ss	1.14E-02	RCCA-5	3.85E-01				
DER-9 ss	1.97E-00	RCCA-7					
RCCA-8	6.59E+04	RCCA-8	8.16E+04			RCCA-8	5.20E+03
		RCCA-8	7.81E+04				

Table 5.5 Comparison of Empirical and Calculated Curie Contents for ^{94}Nb

Activity in Ci/m^3

		Migliore et al					
This work		Laboratory Results		ORIGEN2 - Calculated		MCNP - Calculated	
Sample ID	Activity	Sample ID	Activity	Sample ID	Activity	Sample ID	Activity
		Control Rod Blade Assembly (CRB)					
DER-1(c)	6.20E-00	C-3	2.25E-01	CRB Top 1/4	6.59E-02		
DER-2(c)	6.20E-01	C-6	8.72E-02	CRB 3rd 1/4	4.97E-02		
DER-3(c)	9.20E-03	C-9	1.03E-03	CRB Bottom 1/4	1.50E-02		
		C-9 (duplicate)	2.30E-03				
		Burnable Poison Rod Assembly (BPRA)					
DER-4 outer	1.30E-01	BPRA-6	9.04E-02	BPRA-6	4.14E-01	BPRA-6	4.53E-02
DER-4 inner	3.61E-01						
		Reactor Rod Cluster Control Assembly (RCCA)					
DER-10A	4.35E+00	RCCA-8	6.26E-02	RCCA	9.98E-01	RCCA-8	1.46E-02

6 Radioactive Waste Disposal Considerations

The report by Migliore et al. (1994) has provided a very detailed analysis of these three spent control rod assemblies (or Non-Fuel Assemblies (NFA)) with respect to their classification according to 10 CFR Part 61.55. The report has discussed the use of volume averaging for disposing of these spent control rods. It also notes "...that some NFA components may not need to be classified. Many NFA components, such as the BPRA and RCCA, fit into a fuel assembly. If a host assembly is available, it would likely be most effective to dispose of them together, since spent fuel assemblies are considered high-level waste and will have their own repository. However, there will not always be a host assembly for every NFA component requiring disposal. In addition, many NFA components, such as the CRB, do not fit within an assembly. In these cases, it is necessary to perform the proper classification."

Based on the analysis in the Migliore et al. report, wherein only the cladding (stainless steel) and some other structural pieces were analyzed, each of the spent control rod assemblies has been classified according to 10 CFR Part 61.55. Their conclusions for the BPRA were that the top fourth of the assembly (hold down assembly and thimble plugs) would be considered Greater than Class C (GTCC) and the three equal sections of the poison rods would be Class C waste. If all four sections were placed in one package, the package would be classified as Class C.

The RCCA was divided into four sections for classification purposes with the top three sections being classified as Class A (maybe Class B depending on the short-lived nuclides present) and the bottom section classified as Class C. If all four sections were packaged together, the package would be considered Class C.

The CRB, if divided into four sections, would have the top three sections classified as Class C and the bottom section that included the velocity limiter as Class A (maybe Class B). If the four sections were packaged together, the package would be considered Class C.

Our analytical data, since it agrees very well with that of Migliore et al. (1994) for the cladding on the spent fuel assemblies, would support their conclusions for the waste classifications for the CRB and the BPRA. The activity content of the boron carbide in the CRB and the glass from the BPRA did not contribute significantly to the activity levels of these assemblies.

However, the presence of ^{108m}Ag in the Ag-In-Cd absorber rod of the RCCA was not acknowledged in the Migliore et al report. Our calculations for the neutron absorber portion of the RCCA indicate a total Curie content on June 1, 1993 of 19.2 Curies. The contribution of ^{60}Co was 7.3 Ci, that of ^{108m}Ag was 10.8 Ci, and that of ^{110m}Ag was 1.1Ci. Therefore, the dominant activity on June 1, 1993 was due to the ^{108m}Ag. Since the ^{108m}Ag has a 130 yr half-life, it will also be the dominant activity even after 100 years of decay. The only other isotope that was measured that would be present in significant quantities after 100 years of decay is ^{63}Ni. Since the activity of ^{63}Ni in pCi/g is a factor of 10 less than that of ^{108m}Ag, one predicts that the ^{108m}Ag will be the dominant activity with time. Figure 6.1 illustrates the change in activity with time for these four isotopes. The absolute values of ^{60}Co, ^{108m}Ag, and ^{110m}Ag were those calculated from the empirical data at the time of the removal of the assembly from the reactor core. For ^{63}Ni, a value of 1 was chosen because the empirically determined values of ^{63}Ni were about a factor of 10 lower than the determined values for ^{108m}Ag.

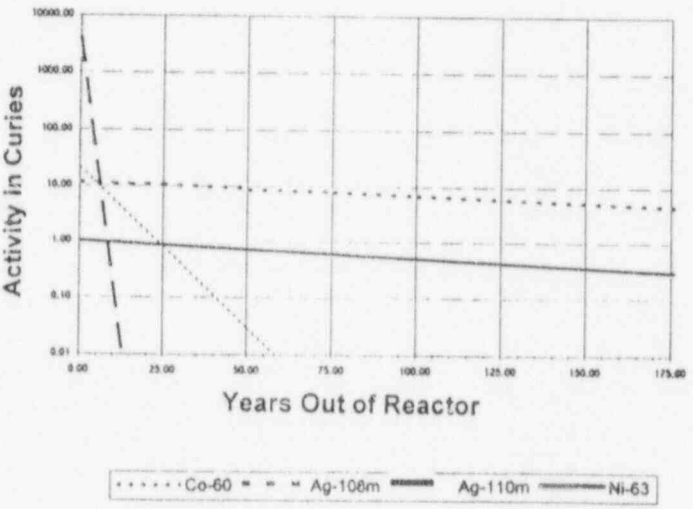

Figure 6.1 Decrease in Concentration with Time for Dominant Isotopes in RCCA

7 Summary and Conclusions

Three different types of control rods were obtained for direct assay measurements and for empirical sampling and analysis. They were: 1) a BWR CRB which consisted of stainless-steel inner tubes and cladding and a neutron poison consisting of boron carbide, 2) a PWR RCCA which consisted of stainless-steel cladding and Ag-In-Cd neutron absorber rods, and 3) a PWR BPRA which consisted of an inner and outer stainless steel tube housing a borosilicate glass tube which served as a neutron poison. Samples were obtained from at least three locations on each control rod, and the radionuclide contents were determined. In the stainless-steel tubes and cladding, the 10 CFR Part 61.55 radioisotopes ^{60}Co, ^{59}Ni, ^{63}Ni, and ^{94}Nb were determined as well as ^{54}Mn, ^{93m}Nb, and ^{93}Mo, ^{125}Sb, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, and ^{155}Eu. In addition, the RCCA also contained ^{108m}Ag, ^{110m}Ag, ^{109}Cd, and ^{113m}Cd in the Ag-In-Cd absorber rod.

Selected samples from each spent control rod assembly were analyzed for their stable element content. The major and minor elements were determined and compared to known compositions for type 304 stainless steel since this was the material used for the cladding and other metal pieces. Our data was consistently high (plus 5% to 34%) in the mass balance that was calculated.

The BWR Control Rod Blade, composed of stainless steel-clad boron carbide, contained predominantly ^{60}Co, which was produced by neutron activation of the nominally 2800 ppm of stable cobalt present in the steel. Nickel-63, ^{93m}Nb, and ^{59}Ni were the next most abundant long-lived activation products, being about 10-fold, 300-fold, and 1000-fold lower, respectively, in concentration compared to ^{60}Co. The ^{94}Nb concentrations averaged about 50-fold lower than those for ^{93m}Nb. The concentrations of the activation products decreased approximately 50-fold from the insert end to the tail end of the neutron-absorbing section of the CRB. The gamma dose rate at the insertion end of the CRB peaked at about 2900 R/h at contact in August, 1990 approximately two years after removed from service. The boron carbide neutron absorber material in the CRB contained relatively low concentrations of all radionuclides, and this material contributed insignificantly to the total radionuclide inventory for the CRB.

The PWR Burnable Poison Rod Assembly, composed of stainless steel-clad borosilicate glass, likewise contained predominantly ^{60}Co, produced from the 1600 ppm of cobalt present in the steel. This steel likewise contained similiar amounts of ^{63}Ni, ^{93m}Nb, ^{59}Ni, and ^{94}Nb, relative to the ^{60}Co, as observed in the CRB. The concentrations of the activation products were rather uniformly distributed over the length of the neutron-absorbing section of the BPRA. The gamma dose rate over this section was about 120 R/h at contact in August, 1990, approximately 15 years after removal from service.

The PWR Rod Cluster Control Assembly is composed of stainless steel-clad rods of an alloy made of 80% Ag, 15% In, and 5% Cd for absorbing neutrons. The radionuclide composition of this assembly is unique, in that the most abundant long-lived radionuclide was ^{108m}Ag. Silver-108m has a half-life of 130 years and decays mainly by electron capture accompanied by the emission of three relatively high energy coincident gamma rays (439, 614, and 722 keV) each of 91% relative intensity. On a per gram basis, the concentration of ^{108m}Ag in this alloy is comparable to the ^{60}Co concentrations in the stainless steel cladding, but the mass of the Ag/In/Cd alloy greatly exceeds that of the stainless steel cladding. Therefore, the ^{108m}Ag will be the dominant gamma dose-contributing radionuclide in this type of control rod assembly for many hundreds of years. Silver-108m is not addressed in 10CFR61, so it cannot be considered in waste classification assessments for this assembly. The RCCA was fully withdrawn at all times during full power operations and only the first few tens of cm on the insertion end of the RCCA were highly neutron activated. The gamma dose rate at the insertion end peaked at about 290 R/h at contact in August, 1990, approximately 10 years after removal from service.

It was possible to directly compare radionuclide measurements for several activation products (^{60}Co, ^{63}Ni, ^{59}Ni, and ^{94}Nb) with samples taken from approximately the same locations on the rod assemblies by another group at PNL (Migliori, et al., 1994). The results of this intercomparison were very good, with general agreement being in the range of 1% to 25%, except for ^{94}Nb where our results averaged about 23 times higher.

Direct assay measurements of the three spent control rod assemblies were conducted in the hot cell facilities at PNL. This technique, which was described in detail in, Robertson, et. al (1993), consists of: 1) direct gamma ray spectrometry to identify those radionuclides contributing to the gamma dose rate, 2) thermoluminescent dosimetry (TLD) to measure the gamma dose rate along the length of the control rod, 3) dose-to-Curie conversion using appropriate shielding/geometry codes, and 4) correlations (scaling) to the ^{60}Co to estimate the concentrations of other 10CFR61 radionuclides in the assemblies. The results of the direct assay measurements were only 10% lower than the empirical measurements for the CRB and the BPRA. The laboratory value for ^{108m}Ag, which was the most abundant radionuclide in the RCCA and contributed to most of the gamma dose, was only 2% higher than the direct assay results, but the ^{60}Co

and ^{110m}Ag laboratory values for the RCCA were a factor of 2.8 higher than the direct assay results. This generally good agreement between the laboratory versus the direct assay measurements of the radionuclide contents of spent control rod assemblies lends confidence that the direct assay methodologies can provide very accurate determinations of the radionuclide inventories of spent control rod assemblies and other types of highly neutron-activated metal wastes.

Calculated radionuclide inventories for these spent control rod assemblies were also determined by a reactor physics group at PNL using both ORIGEN2 and MCNP modeling, and their results were compared with our laboratory measurements. Neutronics modeling calculations are especially difficult to perform for spent control rod assemblies because of the large quantities of neutron absorbing materials in the rods and the uncertainties in their exact position relative to the reactor core over their operational history. The objective of this comparison was to determine how accurate the calculations were relative to the laboratory measurements (assumed to be the more accurate of the two methods). This comparison showed that for the CRB our laboratory values for ^{60}Co, ^{63}Ni, and ^{59}Ni were about 3 to 5 times higher than the calculated values at the insert ("hot") end of the assembly, and at the "cold" end of the assembly our laboratory values were 0.15 to 0.68 times the calculated values. For the BPRA, our laboratory ^{60}Co values were 3.9 times higher than the calculated values, and the laboratory ^{63}Ni and ^{59}Ni values were 0.78 and 0.73 times the calculated values. For the insert end of the RCCA, our laboratory ^{60}Co, ^{63}Ni, and ^{59}Ni values were 3.6, 12.7, and 12.6 times higher, respectively, than the calculated values. These comparisons confirm the difficulty in calculating the radionuclide inventories in spent control rod assemblies. It appears that generally it is possible to perform radionuclide inventory calculations that are within a factor of about 5 of the true values, but occasionally, differences exceeding a factor of ten were observed. Obviously, the direct assay techniques are preferable to the calculational methods for estimating radionuclide inventories of spent control rod assemblies.

The radionuclide inventories of the three spent control rod assemblies were assessed to provide a 10CFR61 waste classification of these materials. If concentration averaging over the entire assemblies is performed, as allowed in 10CFR61.55, then each of the assemblies would be classified as Class C low-level waste, even though the "hot" ends of the CRB and BPRA approached or slightly exceeded the Class C limit. Nickel-63, followed by ^{94}Nb, were the classification-controlling radionuclides. Since the concentrations of these radionuclides are so close to the Class C limit for the these types of activated-metal waste it is important that the determination of their radionuclide contents be determined as accurately as possible.

The information and data bases that have been generated during these radionuclide characterization studies have provided a more comprehensive and reliable assessment of the radiological factors associated with the decommissioning of nuclear reactor power stations.

8 References

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Appendix A: Summary of PNL Radiochemical Procedures for 10 CFR Part 61 and Selected Radionuclides

A.1 Aluminum-26

Aluminum-26 in aliquots of borosilicate glass from burnable poison rods is measured by instrumental analysis. A triple coincident gamma-ray spectrometric technique is used which measures both 511-keV gamma photons from positron annihilation and the 1809-keV gamma photon.

A.2 Cadmium-109,-113m

Cadmium-109,-113m are measured in the Ag-Cd-In alloy of rod cluster control assemblies (RCA) by treating aliquots of nitric acid dissolutions of the alloy with repeated silver chloride precipitate scavenging steps. The supernates from each aliquot are combined and evaporated to dryness. The residues are dissolved in dilute HBr-nitric acid solution and passed through anion columns. The columns are washed and the cadmium is eluted with 2 M nitric acid. The eluates are evaporated to dryness, the residues are dissolved in NH_4OH and adjusted to pH 8 with HCl/NaOH. Cadmium sulfide is precipitated with thioacetamide, filtered, and dried. Cadmium-109 is determined by gamma spectrometry and ^{113m}Cd is determined by beta absorption counting.

A.3 Molybdenum-93

Molybdenum-93 is measured in reactor hardware samples by scavenging acid dissolution aliquots repeatedly with Fe-Co-Ni-Nb hydroxide precipitates from a weak sodium hydroxide solution containing a trace of $NaNO_2$. Molybdenum is then precipitated as lead molybdate. Molybdenum-93 is determined using a thin-window intrinsic germanium detector through measurement of the niobium daughter x-rays. Yields are determined by using ^{99}Mo tracer.

A.4 Nickel-59,-63

Nickel radionuclides are separated from reactor waste by successive steps of chelating iron with citric acid and precipitating the nickel as dimethylglyoxime. The final dimethylglyoxime precipitate is weighed and mounted for measurement of the ^{59}Ni x-rays with a low energy gamma spectrometer. The precipitate is then carefully dissolved in nitric acid and taken to dryness. The residue is dissolved in weak HCl and prepared for beta counting in a liquid scintillation spectrometer for ^{63}Ni. Yields are determined gravimetrically.

A.5 Niobium-93m,-94

Niobium-93m,-94 are measured in neutron-activated reactor hardware, after dissolution of the metal samples, by precipitation of niobic oxide in concentrated nitric acid. Both stable niobium carrier and ^{95}Nb tracer are added during the separation. Niobium-94 is measured by gamma-ray spectrometric techniques while ^{93m}Nb is determined by measuring the niobium x-rays using a thin window intrinsic germanium detector. Yields are determined by measuring the ^{95}Nb tracer by gamma-ray spectrometry.

A.7 Transuranics

Isotopes of americium, curium, and plutonium are separated from acid dissolutions of reactor samples. Aliquots are spiked with ^{242}Pu and ^{243}Am as yield tracers. The solutions are adjusted to 2 M HNO_3 and iron and ascorbic acid are added to complex and reduce iron to Fe(II). TRU-Spec™ resin columns containing octyl(phenyl)-N, N-diisobutyl-carbamoylmethylphosphine oxide are equilibrated with 2 M HNO_3 and the samples are passed through the columns. After washing the columns, americium and curium are respectively eluted with 9 M HCl and 4 M HCl. Plutonium is eluted with 4 M HCl/0.1 M hydroquinone. Small amounts of Nd carrier are added to the plutonium and americium-curium fractions and the fluorides are precipitated and counted by alpha energy analysis.

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11. ABSTRACT *(200 words or less)*

This report describes the results of non-destructive and laboratory radionuclide measurements, as well as waste classification assessments, of BWR and PWR spent control rod assemblies. The radionuclide inventories of these spent control rods were determined by three separate methodologies, including 1) direct assay techniques, 2) calculational techniques, and 3) by sampling and laboratory radiochemical analyses. For the BWR control rod blade (CRB) and PWR burnable poison rod assembly (BPRA), ^{60}Co and ^{63}Ni, present in the stainless steel cladding, were the most abundant neutron activation products. The most abundant radionuclide in the PWR rod cluster control assembly (RCCA) was ^{108m}Ag (130 yr halflife) produced in the Ag-In-Cd alloy used as the neutron poison. This radionuclide will be the dominant contributor to the gamma dose rate for many hundreds of years. The results of the direct assay methods agree very well (±10%) with the sampling/radiochemical measurements. The results of the calculational methods agreed fairly well with the empirical measurements for the BPRA, but often varied by a factor of 5 to 10 for the CRB and the RCCA assemblies. If concentration averaging and encapsulation, as allowed by 10CFR61.55, is performed, then each of the entire control assemblies would be classified as Class C low-level radioactive waste.

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