LOW-LEVEL RADIOACTIVE WASTE FROM NUCLEAR POWER GENERATING STATIONS: CHARACTERIZATION, CLASSIFICATION AND ASSESSMENT OF ACTIVATED METALS AND WASTE STREAMS

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ABSTRACT

Since the enactment of 10 CFR Part 61, additional difficult-to-measure long-lived radionuclides, not specified in Tables 1 or 2 of Part 61, have been identified (e.g., ^{108m}Ag, ^{93}Mo, ^{36}Cl, ^{10}Be, ^{113m}Cd, ^{121m}Sn, ^{126}Sn, ^{93m}Nb) that may be of concern in certain types of waste. These nuclides are primarily associated with activated metal and perhaps other nuclear power low-level waste (LLW) being sent to disposal facilities. The concentration of a radionuclide in waste materials is normally determined by direct measurement or by indirect calculational methods, such as using a scaling factor to relate inferred concentration of a difficult-to-measure radionuclide to another that is easily measured. The total disposal site inventory of certain difficult-to-measure radionuclides (e.g., ^{14}C, ^{129}I, and ^{99}Tc) often controls the total quantities of radioactive waste permitted in LLW burial facilities. Overly conservative scaling factors based on lower limits of detection (LLD), often used in the nuclear power industry to estimate these controlling nuclides, could lead to premature closure of a disposal facility. Samples of LLW (Class B and C activated metals [AM] and other waste streams) are being collected from operating nuclear power stations and analyzed for radionuclides covered in 10 CFR Part 61 and the additional difficult-to-measure radionuclides. This analysis will enhance the NRC's understanding of the distribution and projected quantities of radionuclides within AM and LLW streams from commercial nuclear power stations. This research will also provide radiological characterization of AM specimens for others to use in leach-rate and lysimeter experiments to determine nuclide releases and subsequent movement in natural soil environments. Preliminary scaling factors for the difficult-to-measure radionuclides will be determined for use when waste is not analyzed or when analytical results are near or below the LLD.

PURPOSE AND SCOPE OF RESEARCH:

In research conducted for the Nuclear Regulatory Commission (NRC), Pacific Northwest Laboratory (PNL) is addressing key issues in characterizing and disposing of all long-lived radionuclides of potential concern in activated metal waste and other waste streams from operating power stations. The objectives of this research are 1) to identify additional long-lived (half-lives greater than 5 years) radionuclides of potential concern, not listed in 10 CFR Part 61, that may be present in significant amounts in various types of low-level radioactive wastes and activated metals, 2) to enhance the NRC's understanding of the distribution and projected quantities of additional long-lived radionuclides within activated metals and low-level waste streams from commercial nuclear power stations, 3) to provide radiological characterizations of activated metal specimens to use in experiments by Idaho National Engineering Laboratory (INEL) for determining leach rates of radionuclides from activated metals, and in field lysimeter studies for determining releases and their subsequent movement in natural soil environments, and 4) to determine appropriate preliminary scaling factors for the difficult-to-measure radionuclides to use when waste is not analyzed or when sample results are near or below the lower-limit-of-detection (LLD).

BACKGROUND

The technical requirements for land disposal of low-level radioactive waste, as specified in 10 CFR Part 61, necessitate that specific waste classification and characterization be performed on low-level waste before disposal. Waste classification involves the quantification of specified radionuclides in the waste materials to comply with disposal requirements and site performance objectives. Since 10 CFR Part 61 was enacted, other long-lived radionuclides have been identified (e.g. ^{108m}Ag, ^{93}Mo, ^{36}Cl, ^{10}Be, ^{113m}Cd, ^{121m}Sn, ^{126}Sn, ^{93m}Nb) that are not routinely measured, but which potentially may be of concern in certain types of waste. These radionuclides are primarily associated with activated metal wastes and perhaps other low-level wastes, of which the nuclear power industry is generating increasing amounts, that are going to low-level waste disposal facilities. More comprehensive radionuclide analyses of the various types of activated metal wastes and low-level radioactive waste streams prior to disposal are therefore warranted to insure that these radionuclides do not pose a problem to public health and safety. In addition, the environmental fate of these long-lived radionuclides, once they are disposed of in low-level waste disposal facilities, is of concern. In order to predict the migration of these radionuclides from disposal sites, it is necessary to determine their leaching rates from the various activated metal matrices by simulated or actual waste trench solutions and/or groundwaters.

The concentration of a radionuclide in waste materials is normally determined by direct measurements or by indirect methods, such as scaling factors that relate the inferred concentration of a difficult-to-measure radionuclide to another that is easily measured by gamma-ray spectrometry. For a number of radionuclides (e.g., ^{14}C, ^{129}I, and ^{99}Tc), the scaling

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factors used in the nuclear power industry have been overly conservative since the factors were based primarily on "less-than" values corresponding to the lower-limits-of-detection of the *analytical methods* used by the commercial laboratories performing the analyses. This has not generally influenced the classification status of the waste, but does artificially increase the inventories of ^{129}I and ^{99}Tc within waste containers, and subsequently, the total inventories of these nuclides at disposal sites.

Recent site performance assessment modeling of proposed low-level waste disposal sites (1, 2, and 3) has indicated that the total disposal site inventories of ^{14}C, ^{129}I, and ^{99}Tc are often the controlling factors for the total quantities of radioactive waste permitted in low-level waste burial facilities. Thus, an overly conservative estimate of the concentrations of these isotopes in low-level waste could lead to premature closure of a disposal facility. It is therefore critical that waste generators use the most accurate scaling factors possible so that less conservative, but still reliable estimates of the total quantities of these nuclides hopefully can be made.

RESEARCH WORK PLAN

The research is being accomplished under the following four major tasks:

Task 1 - obtain and analyze waste stream samples for 10 CFR Part 61 radionuclides and additional difficult-to-measure radionuclides

Task 2 - determine scaling factors for difficult-to-measure and 10 CFR Part 61 radionuclides for waste samples analyzed

Task 3 - resolve discrepancies between calculated vs measured concentration estimates of ^{59}Ni and ^{63}Ni in activated metal waste

Task 4 - characterize and transfer activated metal specimens to INEL for to use in leaching experiments and field lysimeter studies.

Literature Review

An extensive survey of literature pertaining to radiochemical analyses of 10 CFR Part 61 radionuclides and several additional long-lived radionuclides (i.e., ^{10}Be, ^{36}Cl, ^{93m}Nb, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, ^{121m}Sn, and ^{126}Sn) expected to be found in nuclear power station waste streams was pursued, and procedures for the radiochemical analyses of these difficult-to-measure radionuclides of interest were adapted for use.

The literature search being conducted throughout the project for procedures used to analyze the 10 CFR Part 61 radionuclides and especially the additional long-lived radionuclides has included several data bases and thousands of references related to these radionuclides and/or their radioactive and stable isotopes. These data bases are being searched for information from 1980 to the present that may be used to enhance existing procedures and that may be adapted to analyze the new radionuclides. Very few of the hundreds of reference abstracts and/or titles retrieved from the data bases appear to be applicable to our purposes. However, many titles and abstracts were selected for further review (by hand screening those resulting from the computer searches) and were passed to the radiochemist adapting the procedures. He has reviewed these journal publications selected from those listings and has identified several candidate procedure improvements.

The Hanford Technical Library (HTL) has used, for this survey, two major literature search vendor services that maintain hundreds of data bases from a broad scope of disciplines: Dialog Information Services, Inc. (Dialog) and STN International (STN). Data bases accessed in Dialog include the following:

- National Technical Information Services (NTIS)
  government-sponsored research, development, and engineering, plus analyses prepared by federal agencies, their contractors, or grantees
- Compendex Plus
  machine-readable version of The Engineering Index, which provides abstracted information from the world's significant literature of engineering and technology
- Energy Science and Technology (formerly DOE Energy)
  one of the world's largest sources of literature references on all aspects of energy and related topics
- Nuclear Science Abstracts
  comprehensive abstract and index collection of all aspects of international nuclear science and technology literature
- Analytical Abstracts
  covers all aspects of analytical chemistry
- Chemical Abstracts Search
  citations from the literature of chemistry and its applications; contains the basic bibliographic information appearing in the printed volumes of *Chemical* Abstracts (no abstracts available).

Databases accessed in STN include the following:

- File CA - Chemical Abstracts
  covers all areas of chemistry and chemical engineering worldwide (STN, unlike Dialog Chemical Abstracts Search, offers an abstract with most of these records.)
- Analytical Abstracts
  covers worldwide literature on analytical chemistry including abstracts for documents reported in the printed volumes of Analytical Abstracts.

Radiochemical Procedures

Radiochemical analysis procedures are in place for all of the 10 CFR Part 61 radionuclides. Tentative procedures for the additional difficult-to-measure radionuclides have been adapted based on past knowledge, experience, and information gleaned from the literature *and personal* contacts. Several of these procedures are being improved by incorporating steps to use a new, more specific, and possibly more sensitive measurement capability now available in our department. A state-of-the-art liquid scintillation spectrometer (Quantulus Model 1220, LKB Wallac Co.) was purchased and delivered to PNL, and is now available to use in this program. This spectrometer provides excellent commercially available liquid scintillation counting with respect to sensitivity, low-background, and resolution. It will be used for measuring pure beta and low-energy-photon emissions from radionuclides

separated from the waste-stream and activated-metal samples in this project. This instrument will enhance the measurement of hard-to-measure nuclides such as ^{99}Tc, ^{63}Ni and ^{59}Ni.

Analytical procedures and measurement methods have been tentatively adapted for the following radionuclides: ^{10}Be, ^{36}Cl, ^{93m}Nb, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, ^{121m}Sn, and ^{126}Sn. The extensive literature search has shown the possibility of incorporating several different solvent extraction and/or ion exchange techniques into these procedures. Tests are presently underway to evaluate which of these techniques might enhance the analytical procedures.

The recently purchased high-resolution low-background beta scintillation spectrometer has added another dimension to measuring many of the radionuclides of interest. With this instrument, for example, we can discern Ni-63 in our Ni-59 standard solution. It may be possible to use this instrument to resolve the energy spectra of these two radionuclides, simultaneously measure both in waste stream samples, and eliminate the electroplating steps necessary for their measurment in a standard beta counter. This instrument has a very high efficiency for measuring monoenergetic electrons and characteristic x-rays emitted during decay by electron capture, internal conversion, and isomeric transition. These low energy electrons and x-rays can be measured down to a few keV. This presents the possibility of using these x-rays and electrons to identify and quantify certain of the hard-to-measure radionuclides.

Following is a brief summary of the tentative analytical procedures:

- **^{10}Be:**

  An aliquot of B_4C with added ^{7}Be as tracer and stable Be as carrier is alkali fused, the residue is dissolved, and $Be(OH)_2$ is precipitated. The precipitate is dissolved in weak HNO_3, and extracted with acetylacetone into chloroform. It is then back extracted into HNO_3. It is reprecipitated as $Be(OH)_2$, dissolved in weak acid and precipitated as $BaBeF_4$. The precipitate is mounted for beta counting followed by beta absorption curve analysis, and then analyzed by gamma-ray spectrometry for ^{7}Be yield. We may also use the Quantulus beta scintillation counter to measure ^{10}Be.

- **^{36}Cl:**

  An aliquot of solid sample is alkali fused with ^{38}Cl tracer and stable chloride carrier. The residue is dissolved in HNO_3. After adding hold-back carriers, AgCl is precipitated. The AgCl precipitation with hold-back carriers is repeated. The sample is analyzed by gamma-ray spectrometry for ^{38}Cl yield, and after the ^{38}Cl (T-1/2 = 37.2 min) has decayed sufficiently, the sample is mounted for beta counting and absorption curve analysis to determine ^{36}Cl. We may also use the Quantulus beta scintillation counter to measure ^{36}Cl.

- **^{93m}Nb:**

  An aliquot of solid sample is alkali fused or alternatively dissolved under controlled conditions in appropriate acid mixtures with ^{95}Nb tracer and stable Nb carrier. The fusion residue is dissolved in HNO_3 and then made strongly basic with NH_4OH, centrifuged, and the precipitate is dissolved in HF. Hold-back carriers and HNO_3 are added, and niobic acid is precipitated by boiling the solution to a smaller volume. The precipitate is dissolved in HF and then niobic acid is reprecipitated. The niobic acid precipitate is mounted for counting, and the ^{95}Nb yield is determined by gamma spectrometry. The niobic acid is then counted for ^{93m}Nb x-rays with a thin-window germanium diode.

- **^{93}Mo:**

  An aliquot of solid sample is alkali fused or alternatively dissolved under controlled conditions in appropriate acid mixtures with ^{99}Mo tracer and stable Mo carrier. The fusion residue is dissolved in HNO_3, and the initial purification is thorough scavenging by precipitation of basic oxidized iron hydroxide. The solution is then passed through an anion resin column, and the Mo is eluted with ammonium acetate. The Mo is precipitated from a nitric acid-bromine water media using alpha-benzoinoxime solution. Molybdenum-99 in the precipitate is measured by gamma spectrometry to determine yield, and the x-rays from ^{93}Mo are measured in a thin-window germanium gamma-ray spectrometer.

- **^{108m}Ag:**

  Silver-108m is determined by gamma spectrometric methods.

- **^{109}Cd, ^{113m}Cd:**

  An aliquot of solid sample with added stable Cd carrier and ^{115}Cd tracer, is alkali fused or alternatively dissolved under controlled conditions in appropriate acid mixtures. The fusion residue is dissolved in HNO_3, and the solution is repeatedly purified, scavenging with AgCl precipitations. Cadmium is extracted from a highly basic solution with dithizone in chloroform, back extracted and precipitated with ammonium phosphate. Cadmium-115 yield is determined by spectrometric gamma ray analysis of the precipitate. Cadmium-115 is allowed to decay, and the precipitate is analyzed by gamma-ray spectrometry for ^{109}Cd followed by beta and/or beta scintillation counting for ^{113m}Cd.

- **^{121m}Sn, ^{126}Sn:**

  An aliquot of solid sample is alkali fused or alternatively dissolved under controlled conditions in appropriate acid mixtures with ^{117}Sn and stable Sn carrier. The fusion residue is dissolved in HCl-NaOCl, and impurities are removed by passing the solution through a cation resin column. Antimony is further scavenged from the HCl solution by extracting it into isopropyl ether. The HCl solution is further scavenged by extracting impurities into ethyl acetate, and finally, Sn is precipitated from the HCl solution with sulfide ion. The tin sulfide precipitate is analyzed by gamma spectrometry for ^{117}Sn for yield, and is then counted by gamma spectrometry and beta scintillation spectrometry for ^{121m}Sn and ^{126}Sn.

Pertinent parameters associated with several long-lived activation-product radionuclides that will be addressed are shown in Table I. If other radionuclides are identified that may contribute significantly to the long-term disposal problem,

they will be added to the list. These radionuclides are expected to be present in significant amounts in certain types of waste streams from commercial nuclear power stations. The waste streams are not presently being analyzed for these radionuclides.

Sampling of Waste Streams and Activated Metal Waste

Assistance has been requested by PNL in procuring samples from 4 waste management vendors and 22 nuclear power stations. We have been fortunate to have received cooperation, at the time of writing, from Waste Management Group, Chem Nuclear Systems, Inc., Limerick Generating Station, Crystal River Nuclear Plant, Unit #3, and Washington Nuclear Project, Unit #2 in obtaining samples of reactor cleanup resins and stainless steel samples. We are continuing communications with vendors and stations to obtain samples of Zircaloy, Inconel, and other waste streams. The NRC has requested that the samples be from actual waste streams on their way (or soon to be shipped) to a low-level waste disposal site. Preferred waste would be classified Type B or C under 10 CFR Part 61. In the case of activated metal, Class C material has relatively high dose rates requiring special handling and shipping. These complications plus the end of the year rush by utilities conducting cleanup campaigns to dispose of waste in 1992 have made it difficult to obtain suitable samples.

REFERENCES

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TABLE I
Additional Radionuclides Expected In Nuclear Power Station Waste

Nuclide	Half-life (Years)	Production Mode	Probable Waste Material
^{10}Be	1.6×10^6	$^{10}B(n,p)^{10}Be$	B_4C control rods
^{36}Cl	3.01×10^5	$^{35}Cl(n,\gamma)^{36}Cl$	activated concrete, B_4C
^{93m}Nb	12	$^{93}Nb(n,n')^{93m}Nb$	activated Inconel, steel
^{93}Mo	3500	$^{92}Mo(n,\gamma)^{93}Mo$	activated steel, Inconel
^{108m}Ag	130	$^{107}Ag(n,\gamma)^{108m}Ag$	Ag-Cd-In control rods
^{113m}Cd	14.6	$^{113}Cd(n,n')^{113m}Cd$	Ag-Cd-In control rods
^{121m}Sn	55	$^{120}Sn(n,\gamma)^{121m}Sn$	activated Zircaloy
^{126}Sn	1×10^5	$^{124}Sn(n,\gamma)^{125}Sn(n,\gamma)^{126}Sn$	activated Zircaloy

Nuclide	Primary Decay Mode	Emission Measured (KeV)
^{10}Be	Beta	555 B^-
^{36}Cl	Beta	709 B^-
^{93m}Nb	Isomeric Transition	28-30 e^- or 16.6 X-ray
^{93}Mo	Electron Capture	28-30 e^- or 16.6 X-ray
^{108m}Ag	Electron Capture	433, 614, 723 gamma photons
^{113m}Cd	Beta	580 B^-
^{121m}Sn	Isomeric Transition	6-7 e^- or 26.4 X-ray
^{126}Sn	Beta	18-23 e^- or 26.4 X-ray