Conf-920851--76

WSRC-MS--92-108

DE92 041346

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A paper proposed for presentation at the
Spectrum '92
Boise, ID
August 23 - 27, 1992

and for publication in the proceedings

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ABSTRACT

This paper presents measurements of the concentrations of 42 of the long-lived U-235 fission products in a high-level radioactive waste sludge stored at Savannah River Site. The 42 fision products make up 98% of the waste sludge. We used inductively coupled plasma-mass spectroscopy for the analysis. The relative yields for most of the fission products are in complete agreement with the known relative yields for the beta decay chains of the two asymmetric branches of the slow neutron fission of U-235. Disagreements can be reconciled based on the chemistry of the fission products in the caustic waste sludges, the neutron fluences in SRS reactors, or interferences in the ICP-MS analyses.

This paper presents measurements of the concentrations of 42 (98%) of the long-lived U-235 fission products in a high-level radioactive waste sludge stored at the Savannah River Site. We analyzed the sludge with inductively coupled plasma-mass spectroscopy. The relative yields for most of the fission products agree completely with the known relative yields for the beta decay chains of the two asymmetric branches of the slow neutron fission of U-235. The chemistry of the fission products in the caustic waste sludges, the neutron fluences in SRS reactors, or interferences in the ICP-MS analyses explain the differences in the measured and calculated results.

INTRODUCTION

The Savannah River Site (SRS) has accumulated approximately 37 million gallons of radioactive high-level waste from producing nuclear materials for defense. SRS stores these high-level wastes as caustic sludges and associated supernates in underground carbon steel tanks. Most of the radionuclides produced by the SRS reactors are insoluble in caustic. Consequently, the sludges contain more radioactivity than the supernates; an exception is radioactive Cs-137, which is soluble in the caustic supernates. The radionuclides are the fission products resulting from slow neutron fission of U-235 (with a small contribution from Pu-239) in the SRS reactors and the transuranic elements not removed by the separations processes for isolating nuclear materials. The major components of the sludges on a mass basis are hydrous oxides of nonradioactive iron, aluminum, and manganese, which are used in the chemical separation and purification processes used at SRS. The supernates contain chemicals that are soluble in caustic; these are primarily nonradioactive sodium hydroxide, nitrate, and nitrite; Cs-137; and small amounts of Sr-90.

SRS is immobilizing waste into borosilicate glass for permanent disposal in a geologic repository. For geologic disposal we must know the concentrations of the long-lived U-235 fission products and the U and transuranic elements. These concentrations indicate the amount of radioactivity in the glass and predict the radioactivity for the repository. This paper reports the first measurement of the concentrations of 42 (greater than 98%) of long-lived U-235 fission products in a radioactive sludge from an SRS waste tank. We used inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and the very sensitive analytical technique of inductively coupled plasma-mass spectroscopy for the measurements. The results are completely consistent with known yields for the various beta decay chains produced by the thermal neutron fission of U-235.

EXPERIMENTAL

We obtained a sample of the radioactive sludge from a high-level waste tank (Tank 15). The sample was dried and then dissolved using hot aqua regia. Because of the high radioactivity of the sludge, we remotely performed this dissolution in a shielded cell. We diluted the final solution and removed a small aliquot from the cell to a radioactive hood, which we further diluted and analyzed for composition. An Applied Research Laboratories Model 3580 spectrophotometer used inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to analyze the major nonradioactive elements; the spectrophotometer has a 27 channel polychromator and a 1 meter Paschen-Runge scanning monochromator. A VG Instruments Plasma Quad spectrometer, which operates in the pulse counting mode, analyzed the solution for fission products and other minor elements by inductively coupled plasma-mass spectroscopy (ICP-MS). Both instruments used RF generated argon plasmas. The plasma sources were in hoods so that radioactive solutions could be analyzed.

RESULTS AND DISCUSSION

Table 1 shows the concentrations of the major components in the tank sludge. Except for Hg and Th, these concentrations were determined using ICP-AES. The composition in Table 1 resembles the nonradioactive compositions for other SRS sludges.[1] The chemical processes at SRS produce most of the nonradioactive elements in the sludge. For example, dissolution of the reactor fuel and target rods produces aluminum and uses mercury as a catalyst; the separation processes use iron as a reductant; and the reactors use thorium and uranium. Chemical compounds of the elements in Table 1 account for more than 99% of the mass of the dried sludge.

Table 1. Major Components of SRS Tank 15 Sludge[a]

Element	Wt. %	Element	Wt. %	Element	Wt. %
Fe	4.9	Ca	0.21	Cu	0.05
Al	30.8	Mg	0.15	Ti	0.02
Na	2.4	Si	0.19	Hg[b]	2.5
Mn	2.5	B	0.01	Th[b]	0.23
U	0.45	P	0.30	Ni	0.46

[a]The sludge was dried at 100°C and dissolved with aqua regia.
[b]ICP-MS results.

Results for the ICP-MS measurements of the U-235 fission products are shown in Figures 1 and 2. These results are presented as relative yields for the various masses detected by the mass spectrometer. Figure 1 shows the relative yields for masses in the range 84 to 111 and Figure 2 shows results for the range 125 to 154. These are the major mass ranges for the two branches of the asymmetric fission of U-235. For the low mass range, the results were normalized to the response at mass 103 The stable fission product Rh-103 has this mass. For the high range, the stable rare earth fission product Pr-141 was chosen as the reference isotope. Also shown in Figures 1 and 2 are the respective relative yields calculated on the same basis using the published values for the various isobaric beta decay chain yields resulting from slow neutron fission of U-235.[2] The measured and calculated yields for the various masses in Figures 1 and 2 cover more than two orders of magnitude. For most of the masses the agreement is very good. The disagreements can b(explained based on the chemistry of the fission products themselves in the caustic waste solutions, the properties of the SRS reactors, and interferences resulting from the ICP-MS measurement.

We chose Rh-103 and Pr-141 for several reasons. They are insoluble in caustic solutions, and they should be present principally in the precipitated sludges and not in the supernates in the SRS waste storage tanks. These elements are not used in any of the processes at SRS and it is highly unlikely that they would be present as significant impurities in any of the process chemicals. Thus their concentrations in the waste should be representative of the amounts of each produced in the SRS reactors. The measured weight percents for these two isotopes in the dried sludge were 0.014 for Rh-103 and 0.030 for Pr-141. Note that these fission product concentrations are much lower than most of the concentrations presented in Table 1.

We identified the most probable radionuclides at the various masses by considering the half lives of the radionuclides in the respective isobaric chains from fission of U-235. In the following tables, we present the radionuclides found at various mass ranges and discuss the disagreements between the calculated and measured results.

Radionuclides Present at the Low-Mass Range

Mass	Product	Comment
84-86	Rb, Kr	Kr is released when the fuel is dissolved, consequently fission products with these masses should not appear in the waste. Some of response at mass 85 may be Rb-85 from decay of Kr-85 while it is in the reactor fuel. If it is Rb-85, its relative yield in the sludge should be low compared to the calculated relative yield because Rb would be soluble in the caustic supernate and would not appear in the sludge.
88	Sr	The result for Sr-88 is slightly high. Since Sr-88 occurs naturally, its relative concentration in the waste tank may be higher than the relative fission yield due to possible Sr impurity in the Na and K hydroxides used at SRS. This natural Sr may also account for some of the responses observed at masses 84, 86, and 87.
90, 91	Sr-90, Y-91	The measured results agree well with the calculated relative yields.
91-94, 95	Zr	In caustic solutions, Zr may be slightly soluble possibly as the zirconyl cation. Thus part of the Zr is in the supernate in the tank. Note that each radionuclide is low by approximately the same amount.
95,97-99 100	Mo, Tc-99	Very soluble in caustic, thus most of these elements are in the supernate. These results have been confirmed by preliminary ICP-MS analysis of the supernate.
101,102,104	Ru	The measured results agree well with the calculated relative yields.
105-108	Pd, Ag	The result for Pd-105 is approximately 10 times low, but the others reasonably agree. We are investigating the low yields of Pd-105.
111	Cd	The measured results agree well with the calculated relative yields.

Radionuclides Present at the High-Mass Range

Mass	Product	Comment
126-136	Xe	There is considerable interference from the Xe impurity in the Ar plasma torch of the ICP-MS and consequently the results are unreliable.
137	Cs	Cs-137 is soluble in the supernate; thus its measured yield is low. However there may be some contribution of Ba-137, a Cs-137 decay product, to this mass. Barium is probably present in the sludge as the carbonate, which is quite insoluble. This accounts for the good agreement of the measured and calculated relative yield for Ba-138.
138-148	Ba-138, La, Ce, Pr, Nd, Sm-147, Sm-148	The measured results agree well with the calculated relative yields.
149, 151	Sm	The measured relative yields for both are very low compared to their calculated relative yields. These nuclides are apparently transmuted to Sm-150 and Sm-152 in the large neutron doses that were present in the SRS reactors. Sm-149 has a neutron cross section of 4.1×10^4 barns while that for Sm-151 is 1.5×10^4 barns.[3]
150,152-154	Sm, Eu-153	The relative yields for the stable isotopes Sm-150 and Sm-152 are slightly high possible due to neutron capture by Sm-149 and Sm-151. The results for Eu-153 and Sm-154 and are also slightly high, possibly due to oxide formation by lower lanthanide elements in the ICP-MS plasma.

CONCLUSIONS

The results presented in this paper indicate that ICP-MS techniques are able to measure the yields of long-lived products from the fission of U-235 in reactors. On this basis, the concentrations of long-lived fission products in radioactive wastes for repository storage can be estimated if the concentration of only one fission product such as Rh-103 or Pr-141 is measured. This concentration and the known fission yields allow the calculation of the concentrations of all the other fission products. This includes radionuclides such as Cs-137 and Tc-99 presuming that they are recovered from the caustic supernates and immobilized in the glass. Due to the high burnups of production reactors, this calculation overestimates the concentration of Sm-151, which has a half life of ~93 years. This calculation also estimates the maximum amount of Se-79, a long-lived beta emitter with a fission yield so low that its concentration probably cannot be measured by ICP-MS. We are now measuring the fission products in other radioactive sludges stored at SRS.

ACKNOWLEDGMENT

The information in this article was developed during the course of work under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy.

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3. G. Friedlander, J. W. Kennedy, E. S. Macias, and J. M. Miller, *Nuclear and Radiochemistry*, 3rd ed., p 631, John Wiley and Sons, New York (1981).

FIGURES

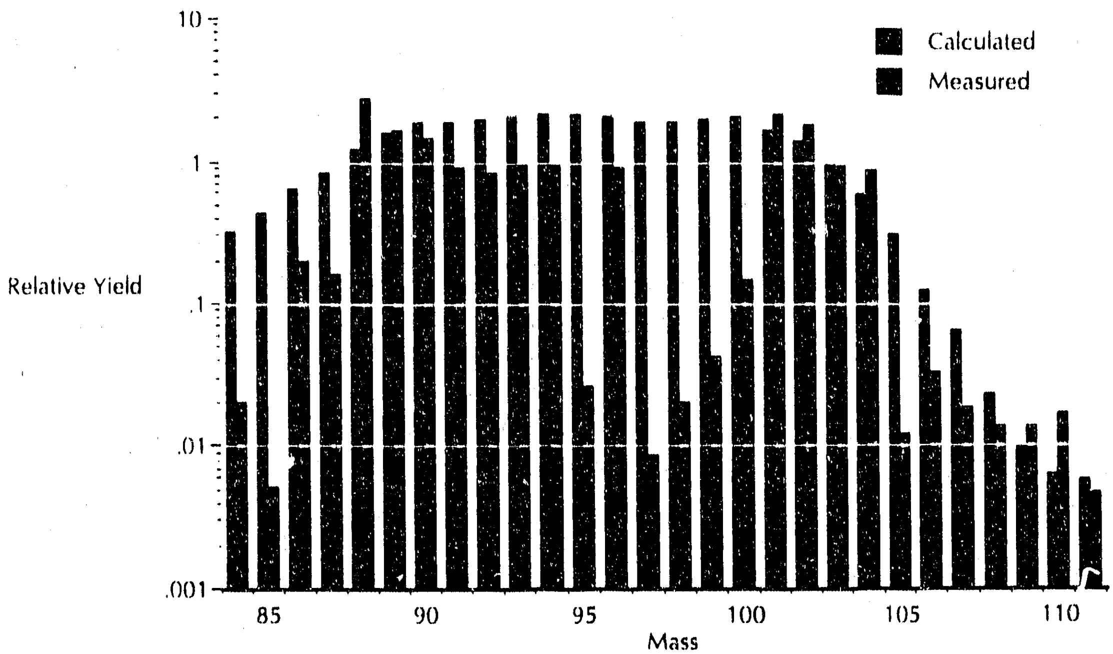

Figure 1. Yields Relative to Mass 103 (Rh-103) for Low Mass Fission Products in Tank 15 Sludge.

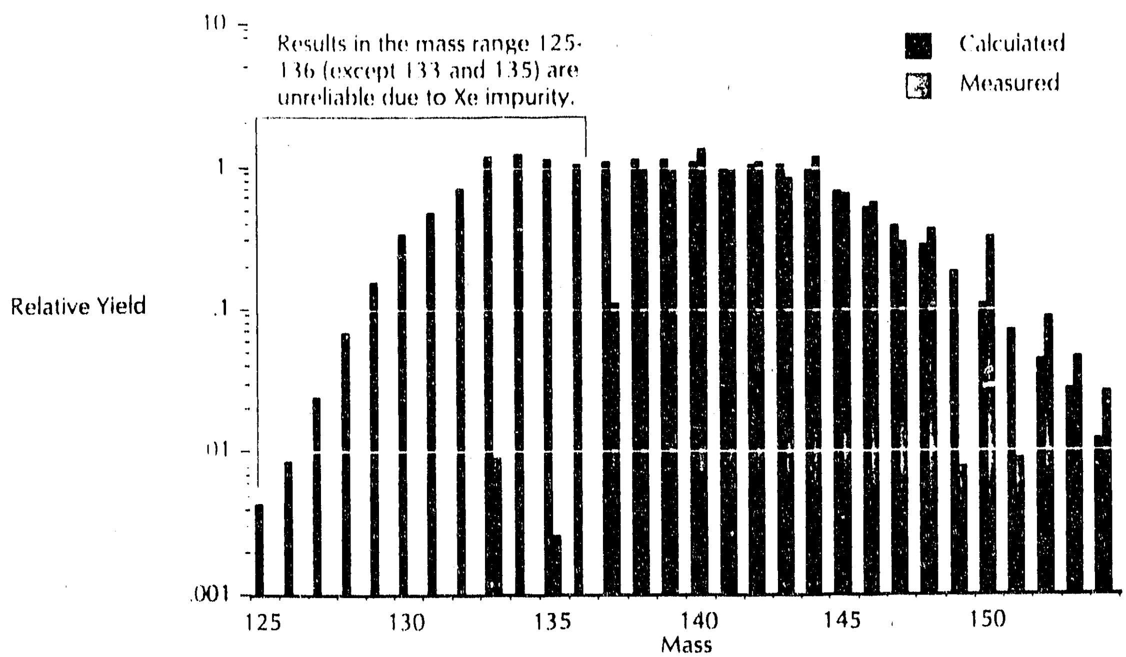

Figure 2. Yields Relative to Mass 141 (Pr-141) for High Mass Fission Products in Tank 15 Sludge.

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June 23, 1992

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WSRC-MS-92-108
ASD-TIM-92-776

Ms. W. F. Perrin, Technical Information Officer
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Remarks See editorial comments on pages 6 and 7. Good idea proposed for obtaining a good estimate of High Level Waste composition at low cost.

W. F. Perrin, Technical Information Officer
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