DETERMINATION OF NOBLE METALS IN SAVANNAH RIVER SITE HIGH-LEVEL RADIOACTIVE SLUDGE (U)

by

C. J. Coleman, W. F. Kinard, N. E. Bibler, D. F. Bickford, and W. G. Ramsey

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

DISCLAIMER

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DETERMINATION OF NOBLE METALS IN SAVANNAH RIVER SITE HIGH-LEVEL RADIOACTIVE SLUDGE

C.J. Coleman, W.F. Kinard, N.E. Bibler, D.F. Bickford, and W.G. Ramsey

Westinghouse Savannah River Company
Savannah River Laboratory
Aiken, SC 29808

ABSTRACT

High-level radioactive sludge at the Savannah River Site (SRS) will be processed at the Defense Waste Processing Facility (DWPF) into durable borosilicate glass wasteforms. The sludges are analyzed for elemental content before processing to ensure compatibility with the glass-making processes. Noble metal fission products in sludge, can under certain conditions, cause problems in the glass melter. Therefore, reliable noble metal determinations are important. The scheme used to measure noble metals in SRS sludges consists of dissolving sludge with hot aqua regia followed by determinations with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-Mass Spectroscopy (ICP-MS) techniques. ICP-MS is the preferred method for measuring trace levels of noble metals in SRS radioactive waste because of superior sensitivity. Analytical results are presented for the two major types of SRS sludge.

INTRODUCTION

High-level radioactive waste at SRS will be processed into borosilicate glass wasteforms in the DWPF.[1] The waste is currently stored in underground steel tanks with capacities up to 1.3 million gallons. The caustic waste consists of two fractions: sludges that contain most of the fission and activation products, and solutions of water-soluble alkali metal salts that contain most of the ^{137}Cs. The salt solution fraction will be decontaminated by adding sodium tetraphenylborate to precipitate ^{137}Cs along with nonradioactive potassium that is present. The tetraphenylborate salts will then be hydrolyzed with formic acid to yield benzene and an aqueous fraction that contains the ^{137}Cs. After distillation to remove the benzene, the aqueous phase will be combined with the sludge from the waste tanks and borosilicate frit and melted at 1150°C in a joule-heated glass melter. The molten glass will be poured into steel canisters and stored at SRS until a geologic repository is selected for final disposal. Processing of radioactive waste into glass is scheduled to begin in 1992.

Elemental analysis of the high-level radioactive sludge is a crucial DWPF process control measurement. The sludge composition affects the processing characteristics and durability of the borosilicate glass product. Major sludge components such as Fe, Al, and the alkali metals affect the viscosity and liquidus temperature of molten glass. Glass durability decreases with increasing alkali and has been shown to be a function of the free energy of hydration of the elements in glass.[2] To optimize processing characteristics and durability of the DWPF glass product, the Savannah River Laboratory (SRL) has developed several glass-forming frits for processing different SRS sludge compositions.

The noble metal fission products Ru, Pd, Rh, Ag in sludge are of particular interest. It has been shown at other nuclear waste vitrification facilities that under reducing conditions in the melter these metals can accumulate on the sides and bottom of the melter.[3-5] The metals may eventually build up to form a conducting layer that may short-circuit the melter electrodes. The melter would then have to be replaced, requiring several weeks of lost production time.

The noble metal concentration in SRS sludges must be known before they are processed in the DWPF. Fission yields have been used in the past to estimate the noble metal concentration in SRS sludges. Since the noble metal concentration in a particular waste tank is a function of the age and types of sludges added to the tank, there is reluctance to depend solely on estimates of noble metal concentration. The potential drastic reduction of DWPF melter lifetime has made it important to determine the noble metal concentration in each SRS waste tank.

The analytical method used at SRL to measure noble metals in sludge consists of sludge dissolution with hot aqua regia and analysis of the solution by using ICP-AES and ICP-MS methods. Results of these analyses are presented for four SRS sludges. One of the sludges is a blend from several waste tanks and is representative of the initial feed sludge to the DWPF.

EXPERIMENTAL

Preparation of Radioactive Sludges for Analysis

Sludge samples from Tanks 51, 4, 11 and 15 were dissolved in the SRL Shielded Cell Facility by heating 0.2 g of the dried sludge and 12 ml of aqua regia at 110°C for two hours in sealed Teflon containers designed for high-pressure digestions. The resulting solutions were diluted to 50 ml with deionized water. A 10 ml portion of each solution was transferred to a radiochemical hood. Tank 51 sludge contained a relatively low level of radiation and was analyzed by ICP-AES without further dilution. Sludges from Tanks 4, 11, and 15 were too high in beta-gamma activity after the initial dissolution to be analyzed in an unshielded hood. These sludges were diluted by a factor of 11 with deionized water and then analyzed by using ICP-AES. Because of the high sensitivity of ICP-MS, the diluted sludges were diluted by an additional factor of 10 before analysis to further reduce radiation.

Complete sludge dissolution was checked by determining the effect of filtering the dissolved samples on the results. Some of the dissolved sludge samples were analyzed both before and after passing them through a 0.45μm pore size filter. Identical results were obtained, indicating that the sludge had been completely dissolved. The hot aqua regia dissolution of SRS sludges provides a suitable matrix for elemental determinations. SRL also frequently uses a Na_2O_2 -NaOH fusion in a Zr crucible to dissolve sludge.[6] The fusion technique was not used to dissolve sludge for the noble metal determinations because the matrix affects both ICP-MS and ICP-AES performance. The ICP-MS technique is affected by the high-alkali matrix and Zr that dissolves from the crucible. The sensitivity of ICP-AES determinations deteriorates due to the increased spectral background from the high-alkai matrix. A final reason for not using the fusion dissolution is that volatile analytes such as Ru would be lost in the 600°C fusion.

Preparation and Analysis of a Synthetic Sludge Containing Noble Metals

A simulated, nonradioactive sludge containing a known concentration of noble metals was dissolved with hot aqua regia and analyzed concurrently with the waste tank sludges to serve as a quality control standard. The simulated sludge was spiked with chloride salts of the noble metals to produce the following noble metal concentrations on a dried sludge basis: Ru, 0.22 weight%; Pd, 0.076 weight%; Rh, 0.047 weight%; and Ag, 0.014 weight%. Determinations within 10% of the known concentration of noble metals were obtained by using both ICP-AES and ICP-MS techniques. Accurate determinations of the sludge standard indicated that the dissolution method and the instrumental calibration techniques were in control during the waste tank sludge analyses.

Instrumentation

ICP-AES determinations were made with an Applied Research Laboratories Model 3580 spectrometer with a 27 channel polychromator and a 1 meter Paschen-Runge scanning monochromator. Analytical channels were available in the polychromator for Ru (240.27 nm) and Ag (328.07 nm). The scanning monochromator was used for analytical lines for Rh (343.49 nm) and Pd (360.96 nm).

ICP-MS determinations were made with a VG Instruments PlasmaQuad spectrometer operated in the pulse counting mode.

RESULTS AND DISCUSSION

Determination Of Major Sludge Elements by ICP-AES

ICP-AES was used to analyze the sludges for the major elements (0.1 weight percent or greater). The elemental compositions (Table 1) show that Tank 51 and 4 sludges have the high Fe content characteristic of sludge produced by the SRS Purex process to separate 238U and 239Pu. Tank 11 and 15 sludges result from the SRS Heavy Metal (HM) process to reclaim 235U from reactor fuel rods. These sludges contain high concentrations of Al and Hg from the Hg catalyzed dissolution of the U-Al fuel rods. Purex and HM process sludges represent the compositional extremes of SRS sludges that will be processed by the DWPF. They were chosen for initial analyses with the goal of bracketing the sludge matrices and noble metal concentrations. Tank 51 sludge, which consists of blended sludge from several tanks, is of particular interest because it is representative of the sludge feed for the first two years of DWPF operation. Tank 51 sludge has been previously analyzed for elemental and radionuclide content.[6] All SRS sludges contain significant concentrations of fission products ^{90}Sr, ^{137}Cs, and [125]Sb along with neutron activation products ^{60}Co, [238]Pu, and [244]Cm.

INSERT TABLE 1

Determination of Noble Metals by ICP-AES

The key to obtaining reliable noble metal determinations in radioactive defense waste samples, as previously discussed by Leutenberger and Hara[7] and West, et.al.,[8] is careful correction for background and spectral interferences. To measure matrix interferences from nonradioactive sludge, a synthetic sludge containing no noble metals was analyzed. The signals were measured that resulted from the synthetic sludge matrix and dissolution

chemicals. This procedure was then repeated with an aliquot of the sludge that contained a spike of the noble metals. By subtracting the matrix signal from the total signal, accurate noble metal determinations were obtained. This simple approach for measuring noble metals in nonradioactive matrices has been successfully applied to other SRL research programs.

Actual radioactive sludges are considerably more difficult than synthetic sludges to analyze with ICP-AES techniques because the complex matrix interferes with noble metal analytical lines. SRS sludges contain many transition metals and lanthanide and actinide series elements with complex emission spectra that interfere with noble metal analytical lines. For example, Tank 51 sludge contains 23.1 weight percent Fe, which interferes at the Ru 240.3 nm line. Tank 51 also contains 2.1 weight percent U, which interferes with the Rh 343.5 nm analytical line. Tank 15 contains 0.23 weight percent Th, which interferes with Pd. The Sm in SRS sludge, though a minor component, severly interferes (154 % interference) with Pd determinations. These interferences result in positive biases to noble metal determinations unless careful corrections are made.

Mathematical corrections were made to attempt to deal with these interferences. The percent spectral interferences were measured by aspirating 1000 ug/ml single-element, high-purity standards of the interfering elements and measuring the signal at the noble metal analytical lines. These measurements were made immediately after the radioactive sludge solutions were analyzed. Line coincidence tables[9] were consulted to help identify possible interferents. Spectral interference corrections were made by subtracting the product of the interferent concentration and the percent interference from the total noble metal concentration. The concentrations of major sludge elements were determined by ICP-AES. The concentrations of most lanthanide and actinide series elements were comparable to that of the noble metals. ICP-MS, because of its superior sensitivity, was used to measure these elements.

The ICP-AES method detection limit for determining noble metals in SRS sludge is a function of the analytical line sensitivity and the sample dilution. The detection limit for Ag in Tank 51 sludge was estimated at 0.0002 weight percent (on a dried sludge solids basis). The detection limit for Ru, Rh, and Pd in Tank 51 sludge is about 0.002 weight percent, because the analytical lines used for these elements are on the order of 10 times less sensitive than the Ag line. The detection limits for measuring noble metals in Tank 4, 11, and 15 sludges are higher by a factor of approximately 10 because of the dilution required to reduce the intense radiation from these samples.

The noble metal concentrations in the sludges as determined by ICP-AES are compared with ICP-MS determinations in Table 2. There was good agreement between the two methods for Ru determinations. This was expected since Ru is found at higher concentrations in SRS sludges than the other noble metals. ICP-AES determinations are relatively less affected by background and spectral interferences as the analyte concentration increases. The concentrations of Rh and Pd in the sludges are relatively low, and the agreement between ICP-AES and ICP-MS is poorer for these determinations. When the two methods disagreed in results, the ICP-MS results were considered to be more reliable because of its superior sensitivity. The ICP-AES results tend to be higher than the ICP-MS results, which indicates that interference corrections were inadequate. The ICP-AES determinations of Tank 15 were unusually high relative to the ICP-MS results. Tank 15 sludge was unique among the sludges analyzed in having a significant concentration of

Th. Since corrections were made for the Th in the sludge, it appears that interferences that were not accounted for contributed to the bias. Ag determinations were in reasonable agreement except for Tank 15 sludge, in which a positive bias was again obtained.

INSERT TABLE 2

Determination of Noble Metals by ICP-MS A mass concentration calibration function was generated by analyzing solution standards containing a mixture of elements over a wide mass range. The instrument software used this calibration function to generate a mathematical calibration function which quantifies the signal at any mass from the response of a single mass of known concentration. A 100 ppb indium spike was added to all samples to serve as a mass calibration marker and a concentration response standard. The concentration response function was verified by analyzing a solution containing a known concen-tration of noble metals.

The data analysis software of the instrument was modified since SRS radioactive sludge does not have a natural isotopic distribu-tion of elements. Masses not usually found in natural samples (i.e., 239, 240, 241, etc.) were added to the data base. The calculation of the concentrations of non-standard isotopic abundances then involved assigning mass abundances of 100% for each mass and assigning the isotopes to an element. The elemental concentration could then be calculated by summing all of the individual mass contributions for the element.

The challenge of this approach was to correctly assign masses to elements. For example, the response at mass 100 could result from Ru, Mo, or a long-lived radioisotope undergoing beta decay. The mass 100 response was assigned as stable 100Mo after considering that the beta decay path of 235U slow neutron fission has no long-lived radioisotopes and that formation of stable 100Mo blocks any further beta decay to 100Ru. Similarly, the mass at 107 was assigned to long-lived 107Pd (t1/2= 6.5 x106 years) rather than stable 107Ag. Based on beta decay systematics, masses at 101, 102, and 104 were assigned to Ru; 103 to Rh; 105, 106, 107, 108 and 110 to Pd; and mass 109 to Ag. A careful analysis of the data must be done to ensure that no large amounts of stable material is present in the tank that might interfere with the beta decay products. In the case of Tank 51 sludge, the data indicated that a substantial amount of stable Ag (masses 107 and 109) and Cd (masses 106, 108, and 110) would interfere with the determination of Pd. In this case, the amount of Pd was calculat-ed by multiplying the concentration of mass 105 by the fission yield for all paths leading to Pd formation divided by the fission yield producing mass 105.

Comparison of ICP-AES and ICP-MS Methods for Noble Metals

ICP-MS is considered to be superior to ICP-AES for analyzing SRS radioactive sludges for noble metals. The most important advantage of ICP-MS is its sensitivity, which is on the order of 100 times better for noble metals than ICP-AES. Sludges can be diluted by a large factor to reduce radiation exposure without affecting the quality of ICP-MS determinations. These same dilution factors would reduce the noble metal concentration below the detection limit for most sludges. Matrix interferences must be corrected to obtain accurate values from both techniques. However, the isobaric interference corrections and mass assignment operations required to obtain ICP-MS results can be performed more reliably than spectral interference corrections. In addition to noble metal determinations, ICP-MS also provides isotopic information and trace level determinations of lanthanide and actinide series elements in radioactive sludge.

Work is now underway to use ICP-MS techniques to measure the noble metals and other minor components in all SRS sludges as a precursor to DWPF operations. A key objective of this program will be to compare the determinations with the concentrations predicted from fission yields. These methods will also be extended to glass matrices to measure noble metals and other trace components in DWPF glass.

CONCLUSIONS

The results of this paper support the following conclusions:

1. ICP-MS is an excellent method for analyzing highly radioactive caustic sludges. It appears to be superior to ICP-AES for these determinations because of its sensitivity. Also, isobaric interferences can be managed more readily than the spectral interferences inherent with ICP-AES determinations. ICP-MS determinations must be corrected for non-standard isotopic abundances to optimize accuracy.

2. ICP-AES is a viable method for determining Ru and Ag in SRS sludge when their concentrations are several times higher than the detection limit. Determinations of Rh and Pd were biased high probably because of inadequate corrections for spectral and matrix interferences. ICP-AES is effective for measuring noble metals in nonradioactive synthetic sludge when analysis of sludge blanks can be used to correct for background and spectral interferences.

ACKNOWLEDGEMENTS

REFERENCES

1. R.Maher, L.F. Shafranek, J.A. Kelley, and R.W. Zeyfanf, "Solidification Of Savanna River High-Level Waste," American Nuclear Society Transactions, 39, p.228, 1981.

2. M.J. Plodinec, C.M. Jantzen, and G.G. Wicks, "Stability of Radioactive Waste Glasses Assessed from Hydration Thermodynamics,"Scientific Basis for Nuclear Waste Management, VII, G.L. McVay (ed.), North-Holland, NY, 755-762 (1984).

3. N. Sasaki, et al, "Solidification of the High-Level Liquid Waste from the Tokai Reprocessing Plant" ANS Inter. Meeting Fuel Reprocessing & Waste Management, Jackson, WY, August, 1984.

4. J.B. Morris, et al "Electrode Corrosion and Ruthenium Behavior in a Small Joule Ceramic Melter", AERE R 12349, October, 1986.

5. M. Stehle, Deutsche Gesellschaft fur Wiederaufarbeitung von Kernbrennstoffen mbH (DKW), Presentation at the Battelle Pacific Northwest Laboratory, April, 1987.

6. C.J. Coleman, N.E. Bibler, and R.A. Dewberry, "Analyses of High-Level Radioactive Sludges and Glasses At the Savannah River Site", Proceedings of the Symposium on Waste Management at Tucson, Arizona, pp 652-657, February, 1990.

7. A.W. Lautensleger and F.T. Hara, "Techniques for the Quantitative Analysis of Fission Product Metals," Battelle Pacific North-west Report No. PNL-3986, August, 1982.

8. M.H. West, C.S. Homi, and C.H. Hunter, "Measurement of Rhodium and Palladium in Selected Hanford Defense Was.es," Analytical Spectroscopy-Proceedings of the 26th Conference on Analytical Chemistry in Energy Technology Knoxville, TN, pp. 203-211, October, 1983.

9. P.W.J.M. Boumans, "Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectroscopy", Pergamon Press, 1980.

TABLE 1: ICP-ES/MS ANALYSES OF MAJOR ELEMENTS IN FOUR SRS RADIOACTIVE SLUDGES

(ELEMENTAL WEIGHT PERCENT[a])

TANK NUMBER

ELEMENT	51 [b]	4	11	15
Fe	23.1	24.3	3.6	4.9
Al	6.4	1.8	23.6	30.8
Na	3.4	12.1	7.9	2.4
K	2.4	0.0	0.0	0.0
Mn	2.3	1.4	1.9	2.5
U	2.1	6.2	0.07	0.045
Ca	1.7	0.64	0.13	0.21
Mg	0.85	0.06	0.18	0.15
Si	0.75	0.02	0.21	0.19
B	0.72	0.01	0.01	0.01
P	0.34	0.29	0.08	0.30
Ni	0.32	5.2	0.77	0.46
Cu	0.28	0.07	0.04	0.05
Ti	0.23	0.01	0.01	0.02
Cr	0.14	0.12	0.02	0.02
Hg[c]	0.02	0.03	4.5	2.5
Th[c]	0.03	0.001	0.005	0.23

[a] Sludges were dried at 100°C and dissolved with aqua regia. Average results of triplicate dissolutions are presented. Relative precision is 5-10%.

[b] Hydrolyzed tetraphenylborate precipitate had been added to this sludge. This accounts for the higher values of K, B, and Cu.

[c] ICP-MS results.

TABLE 2

DETERMINATIONS OF NOBLE METALS IN SRS SLUDGES

BY ICP-MS AND ICP-AES

		CONCENTRATION[a] IN WT.%			
		Ru	Rh	Pd	Ag
Tank 51	ICP-MS	0.005	0.0008	0.0004	0.010
	ICP-AES	0.002	0.002	<0.002	0.014
Tank 4	ICP-MS	0.115	0.025	0.006	0.002
	ICP-AES	0.119	0.030	<0.02	0.002
Tank 11	ICP-MS	0.099	0.022	0.005	0.0007
	ICP-AES	0.093	0.035	<0.02	<0.002
Tank 15	ICP-MS	0.064	0.013	0.002	0.0003
	ICP-AES	0.077	0.055	0.15	0.004

a. Weight % of the dried sludge.

END

DATE
FILMED
4 129192