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**ANALYSES OF HIGH-LEVEL RADIOACTIVE GLASSES AND SLUDGES AT
THE SAVANNAH RIVER SITE (U)**

by

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ABSTRACT

Reliable analyses of high level radioactive glass and sludge are necessary for successful operation of the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS). This facility will convert the radioactive waste sludges at SRS into durable borosilicate glasses for final disposal in a geologic repository. Analyses that are crucial to DWPF operation and repository acceptance of the glass are measurement of the radioactive and nonradioactive composition of the waste sludges and final glasses and measurement of the Fe(II)/Fe(III) ratio in a vitrified sample of melter feed. These measurements are based on the remote dissolutions of the glass and sludge followed by appropriate chemical analyses. Glasses are dissolved by a peroxide fusion method and a method using HF, HNO₃, H₃BO₃, and HCl acids where the solutions are heated in a microwave oven. The resulting solutions are analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS) for nonradioactive elements and appropriate counting techniques for radioactive elements. Results of replicate samples of a standard simulated nuclear waste glass indicate a precision of

5% or better for the major components. The results agree well with the standard values indicating good accuracy. Results for two radioactive glasses containing actual radioactive waste are also presented. Sludges are dissolved by the Na_2O_2 fusion method and an aqua regia method. Analyses of replicate sludge samples indicate that the results have a precision of nominally 5% or better for the major components. Standard sludges are not available to test the accuracy of the methods; however, results of the standard glass analyzed concurrently indicate that the analyses are accurate. Also, results of the two methods for the sludge are in excellent agreement, further indicating that they are reliable and accurate. The Fe(II)/Fe(III) ratio in a radioactive glass sample can be determined colorimetrically using fiber optics after dissolving the glass in HF and H_2SO_4 acids.

INTRODUCTION

In 1992, the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) will begin solidifying high level radioactive defense waste slurries at SRS [1]. The waste, primarily a caustic sludge, will be combined with glass-making chemicals in the form of a frit and melted at 1150°C to form borosilicate glasses for permanent disposal. Advantages of this vitrification process include immobilization of radionuclides in a durable glass waste form for safer storage and elimination of the need for fabricating costly new waste tanks at SRS.

The DWPF will have an at-line laboratory for performing analyses critical for process and quality control. The laboratory will have a process sampling cell, three shielded analytical cells, an instrumentation and chemical separation module, and a counting room for radioactive analyses. High radiation samples can be analyzed directly in the shielded cells or prepared and diluted for

analyses in the instrumentation laboratory.

The Savannah River Laboratory (SRL) has for several years tested in its Shielded Cell Facility the major DWPF processes using actual radioactive sludge. To support these tests, two shielded cells were equipped for remote analyses. The analytical methods proposed for use in the DWPF were then tested to ensure their reliability, precision, and accuracy for supporting the DWPF. The tests were also designed to assess the durability of remote analytical equipment in a radiation environment.

Accurate analyses of the radioactive glass and the waste tank sludge are essential for DWPF process and quality control. Sludge composition must be known to design a frit that can be blended with the sludge to facilitate processing and to optimize glass durability. For example, glass samples will be analyzed for radioactive and nonradioactive elemental composition. Also, the Fe(II)/Fe(III) ratio of the vitrified melter feed sample will have to be determined to predict the relative redox conditions of the glass melt prior to feeding the large batch to the melter. The elemental composition of this vitrified sample will also have to be determined to verify that process streams were blended correctly to produce durable glass. Radionuclide measurements in the sludge and glass will be necessary to comply with specifications for the glass prior to its acceptance by a federal repository [2].

This paper discusses the remote dissolution techniques used for both glass and sludge. Results of analyses are presented for a standard simulated nuclear waste glass, for radioactive glasses containing actual radioactive waste sludge, and for a sludge prior to vitrification. These results indicate the precision and accuracy that can be expected for the process and quality control analyses. Results are also presented for measurements of the

Fe(II)/Fe(III) ratio in radioactive nuclear waste glass.

REMOTE ANALYTICAL METHODS

Dissolution Methods For Glass and Sludge

Glass and sludge are dissolved by two methods to yield solutions suitable for elemental and radionuclide analyses. Results of independent dissolutions are assessed separately to provide a useful cross-check for most elemental and radionuclide determinations. The solutions are analyzed for nonradioactive elements using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS). Radionuclides are measured by conventional alpha, beta, and gamma spectroscopy and counting methods. For minor radionuclides, special chemical separations are required to separate them from the major radioactivity in order to get accurate measurements. Each of the dissolution methods and their relative merits will now be discussed.

Sodium Peroxide Fusion Dissolution of Glass and Sludge

A sodium peroxide fusion effectively dissolves both sludge and glass. About 0.25 g of finely crushed sample is heated with 2.5 g of sodium peroxide in a covered nickel or zirconium crucible for 10 minutes at 700°C. Deionized water and concentrated hydrochloric acid are added to dissolve the mixture after fluxing. The major disadvantage of this method is that it cannot be used to determine sodium. The method also results in a relatively high concentration of dissolved solids and acid that can affect nebulizer performance in ICP-AES and AAS determinations.

Microwave-Acid Dissolution Of Glass

A microwave oven dissolution procedure is used to dissolve glass for elemental analysis [3]. A mixture of 0.25 g of finely crushed glass and 5 ml each of concentrated HF and HNO₃ are heated at 40% microwave power for 12 minutes. After cooling, 40 ml of a 0.6 M boric acid solution is added to complex fluoride ion. The final step is addition of 5 ml of concentrated HCl and heating at 40% microwave power for 5 minutes. The solution is diluted and then analyzed using ICP-AES and AAS techniques. This method yields solutions that can be analyzed for all of the components of interest in SRS glass except boron and silicon. Boron determinations are precluded by the addition of boric acid. Silicon can be accurately determined from this solution only if the ICP-AES torch and spray chamber assembly are fabricated of silicon-free materials. This assembly at SRL is quartz, which can be attacked by free fluoride. Thus, silicon is obtained from the sodium peroxide fusion.

The microwave dissolution oven used for SRL analyses has operated in a shielded cell in a radiation environment for three years with no malfunctions. The oven was modified for remote operation. The switches and other electronic components to a module located conveniently outside the cell to increase the lifetime of the oven in a high radiation field. A similar scheme was used to remote a microwave oven-balance system used for measuring the weight percent solids of DWPF slurries.

Aqua Regia Dissolution of Sludge

For this dissolution method, 0.2 g of dried sludge is heated with 12 ml of aqua regia for two hours at 110°C in a sealed reaction vessel. The reaction vessel is a commercially available

Teflon container especially designed for high pressure digestions. A conventional drying oven is used to heat the mixture. Microwave heating cannot be used because it may result in sample loss due to excessive pressure buildup in the container. The aqua regia dissolution method is effective for dissolving SRS sludge slurries for subsequent analyses and measurement of nearly all the major radioactive and nonradioactive elements in SRS waste. However, comparison of Si values obtained from the aqua regia and Na₂O₂ dissolutions indicates that Si dissolution is incomplete in aqua regia.

Fe(II)/Fe(III) Ratio Measurements

The Fe(II)/Fe(III) ratio in glass is a measure of the redox conditions in the molten glass in the melter. These conditions affect the performance and lifetime of the joule heated melter. Excessive reducing conditions result in precipitation of nickel sulfide and noble metals that can short-circuit the melter electrodes. If the conditions are too oxidizing, excessive foaming can result, limiting the melter feed rate.

The Fe(II)/Fe(III) ratio in glass was determined with a colorimetric technique previously reported by Baumann (4). Absorbance measurements were made with a photodiode array spectrophotometer. Van Hare and Prather (5) adapted the spectrophotometer for remote operation by using fiber optic cables to transmit light from the source to the sample cuvette and back to the detector. The only components in the shielded cell are the sample cuvette, a peristaltic pump for filling the cuvette, and the fiber optic cables. The spectrophotometer and the control switch for the peristaltic pump were located outside the cell for easy access and maintenance.

RESULTS AND DISCUSSION

Analyses of a Standard Simulated SRS Nuclear Waste Glass

Determination of the composition of the radioactive glass is critical to process control in the DWPF and to ensuring that the glass will be accepted by the repository. Consequently, the methods used must be accurate and precise. Much work was performed at SRS to adapt the Na_2O_2 fusion and microwave-acid dissolution techniques so they could be performed remotely in a hot cell environment. It was found that the microwave-acid wave technique was more reliable because it was a sealed dissolution method which minimized contamination of the sample with radioactivity or other contaminants in the cell. Consequently, this method is used at SRS for all elements except Si and B. Boron is added as a reagent in the microwave-acid technique and Si often reprecipitates with this technique.

To test the accuracy and precision of the dissolution and analytical methods, six samples of a standard glass were dissolved remotely and analyzed. Table 1 compares the SRS results with those obtained by Corning Glass Works at Corning, NY, who prepared the standard. Their results are based on 5 to 10 analyses performed using hands on procedures. The standard glass has a composition close to that expected for DWPF glass. As seen in Table 3, both laboratories obtained precise results that are in excellent agreement. The results for each oxide differ from each other by less than 4%. This agreement establishes that the dissolution procedures can be performed reliably with manipulators in a hot cell environment.

Analyses of Two Radioactive SRS Nuclear Waste Glasses
Containing Actual Sludge

The concentrations of the major nonradioactive and radioactive components in the two radioactive glasses containing actual sludge are given in Table 2. The compositions of the glasses are different because they were prepared from different sludges and from different frits. The 165/42 glass was prepared using Frit 165 and sludge from SRS Tank 42. This glass contained nominally 28 wt% sludge oxides and 72 wt% frit oxides. Except for Cs-137, the radionuclide concentrations in this glass are close to those expected in actual DWPF glass [9]. The dose rate from this glass was estimated to be approximately 2000 rad/hour using a solid state dosimeter. This dose rate is primarily due to the gamma and beta radiation from Cs-137, Sr-90, and their daughters. The Cs-137 concentration in the 165/42 glass is lower than that expected in the DWPF glass because the actual radioactive waste supernate, which contains ~99% of the Cs-137, was not processed and put into this glass.

The 200R glass was prepared using Frit 200 and a mixture of radioactive sludges from SRS Tanks 8 and 12. The final glass contained nominally 28 wt% sludge oxides, 64 wt% frit, and 8 wt% simulated tetraphenylborate precipitate hydrolysis product. The precipitate hydrolysis product simulates the waste that will result from the in-tank precipitation of Cs-137 to remove it from the salt solution and put it into the glass. This accounts for the presence of K in this glass. The radioactive composition of 200R is significantly lower than 165/42 glass because 200R glass also contained some simulated sludge which diluted the radionuclides.

Both glasses were prepared at SRL in separate campaigns using a remotely operated, slurry-fed, joule heated melter in the

Shielded Cell Facility. In these campaigns, a slurry of frit and waste was fed to the melter at 1150°C. The molten glass was poured from the melter into 500 mL stainless steel cans. Each campaign produced several cans of glass. To obtain samples for analysis, a can for each glass and cut into 0.5" slices. Samples were obtained by knocking pieces of the glass out of these two slices. The glass was crushed and samples dissolved by the microwave-acid and Na₂O₂ dissolution methods.

The results presented in Table 2 are averages of dissolutions of twelve to eighteen samples of each glass. For the major oxides (those >1 wt%) and radionuclides (Cs-137 and SR-90), the relative precision was 6% or better. For the minor components such as NiO, Sb-125, and the alpha emitters, the relative precision was 10 to 20%.

Analyses of a Radioactive Sludge

The radioactive sludges stored in the tanks at SRS have different compositions due to the many chemical process performed at SRS. These sludges are mixtures of nitrate, nitrite, carbonate, sulfate, and hydrous oxide salts and cannot be directly fused into oxide glasses. Thus, a suitable glass forming frit has to be added. This frit will contain large amounts Si and B so that a low melting (<1200°C) borosilicate glass can be produced. As mentioned before, the specific composition of the frit depends in part on the composition of the sludge being vitrified. The analyses of the sludge that are necessary in order to design this frit are those for the metallic and nonmetallic species in the sludge that form oxides in the glass. The results of replicate determinations of the necessary nonradioactive elements for one specific sludge (sludge from SRS Tank 51) are shown in Table 3. Averages and standard deviations for the results for both remote dissolution

methods, the Na_2O_2 fusion and aqua regia, are given. These results are in general agreement with earlier scoping analyses of sludges in several SRS storage tanks [5].

The results in Table 3 indicate the precisions of the sludge dissolution methods. To determine the precision, nine samples of dried sludge were dissolved remotely by each method. The resulting solutions contained no solids and were analyzed by AAS for K and Hg and ICP-AES for the remainder of the nonradioactive elements. (Na and Ni cannot be analyzed in Na_2O_2 fusion solutions due to interferences from the Na_2O_2 and Ni in the crucibles. K and Hg are better determined by the AAS analysis of aqua regia dissolution.) Both dissolution methods yield results that are very precise. The percent relative standard deviations for all the major components are 5% or less.

The accuracies of the two dissolution methods for sludge could not be determined directly since standard sludges of known compositions are not available. To determine the accuracy of the overall analysis, the sludge and a standard glass with a composition similar to the sludge (see Table 1) were dissolved and analyzed concurrently. The dissolution method used was the Na_2O_2 fusion since the aqua regia is not effective for dissolving glass. The results of the glass standard analyses verified that the dissolutions and the ICP-AES and AAS analyses were yielding accurate results. Further, since the results of for all the elements in the sludge measured by both methods are in excellent agreement (Table 3), the aqua regia also yields accurate results. In future dissolutions of sludge, a standard glass that contains the major elements present in SRS sludge will be dissolved and analyzed concurrently as a quality control measure for the analytical laboratory.

SRS sludges contain four elements, Na, B, Si, and Li, that are also present in the frits that will be used. Consequently, the analyses for the amounts of these in the sludge are critical. Na in the sludge results from addition of NaOH to neutralize the acidic process wastes prior to storing them in the tanks. Si results primarily from zeolites used to concentrate Cs-137 in process streams. Only small amounts of Li and B are used in the separation processes at SRS; thus their concentrations are low in the sludge. Tank 51 sludge, contained <0.02% weight percent Li and B. Since the Si, B, and Li concentrations are low in this sludge, only the Na will be common to both the frit and the sludge. The results in Table 1 can then be used to design a frit that will allow this sludge to be fused into a borosilicate glass with properties compatible with DWPF operation and with repository storage.

Results for the radioactive elements analyzed in the dried samples of Tank 51 sludge are presented in Table 4. These radionuclides are those that can be determined directly in the dissolved sludge solutions without using any separation or isolation procedures. They represent only a small fraction (~10%) of the total number of radionuclides that may be present in the sludge [7]. As with the nonradioactive elements, the precision of each dissolution is good, and the results of both methods are in excellent agreement.

The major radioactive element in the sludge is the beta emitting fission product Sr-90. Analyses for this radionuclide in the solutions resulting from the aqua regia dissolution were very imprecise and thus not reported. We feel that this imprecision resulted from interferences in the Chrenkov liquid scintillation technique used to count the beta particles from Sr-90 and its daughter Y-90. Even though the results for the Na₂O₂ dissolution

were very precise, methods to isolate the Sr-90 and check the accuracy of the Chrenkov counting method are in progress.

The radionuclides that can be easily detected by gamma spectroscopy are the fission products Cs-137, Ce-144, and Eu-155, the neutron activation products Co-60 and Eu 154, and the Am-241 that results primarily from decay of Pu-241 in the waste. Gross alpha counting was performed on plates of the evaporated solutions. Alpha pulse height analysis of the activity on the plates indicated that 80% of the total alpha activity was due to Pu-238 or Am-241, 10% was due to Pu-239, and 10% to Cm-244. Based on the result for Am-241 from the gamma spectroscopy (1.4 mCi/100g) and the alpha pulse height results, the major alpha emitter in the waste is Pu-238 with concentration of ~8 mCi/100 g. This concentration is reasonable considering the high specific activity of Pu-238.

Uranium is a relatively large component (3.5 wt. %) of this sludge and could be determined by ICP-AES. To determine its isotopic content total U was isolated by anion exchange and analyzed by mass spectroscopy. The results indicated that it was 99.28% U-238, 0.52% U-235, 0.02% U-234, and 0.04% U-236. This is slightly depleted in U-235 compared to natural U which has 0.72% U-235.

Many minor radionuclides in the sludge must be measured so that the radionuclide content of the glass will be known prior to sending it to a repository [2]. These are all radionuclides that have half lives greater than 10 years and contribute greater than 0.01% of the radioactivity in the glass at any time up to 1100 years. These radionuclide include 24 long-lived fission and activation products. To measure these radionuclides, appropriate separation techniques have to be applied to isolate them from the high levels of activity in the sludge. SRS is now in the process

of developing methods to measure these. Some have already been measured. Actinides were separated from the other radionuclides in three dissolved sludge solutions by an anion exchange procedure. In the resulting solutions, Pu, U, and Cm were detected along with a trace of Np-237. Based on these three samples, the Cm-244 concentration was 1.0 ± 0.1 mCi/100g. This result is in agreement with the pulse height analysis that indicated that ~10% of the alpha activity was due to Cm-244. The Np-237 concentration in the solutions was measured by mass spectroscopy. The results were very imprecise but indicated that in the sludge the Np-237 concentration was in the range 3×10^{-4} to 3×10^{-3} mCi/100g. In order to measure Ni-63, Ni was isolated from the three dissolved sludge solutions by precipitation with dimethylglyoxime. Ni-63 was then determined by liquid scintillation counting. The result was 0.006 ± 0.001 mCi/100g. Ni-63 resulted from neutron irradiation of Ni clad slugs in the SRS reactors. The fission product Tc-99 was measured in three other dissolved sludge solutions after isolating it by solvent extraction. The results were imprecise but indicated that the Tc-99 concentration was in the range 0.02 - 0.2 mCi/100g. Methods for these radionuclides are being improved and methods for the others being developed.

Analysis of the Fe(II)/Fe(III) Ratio in Radioactive Glass

The colorimetric technique for measuring the Fe(II)/Fe(III) ratio was checked using a highly radioactive glass. The colorimetric technique requires that the glass be dissolved in a mixture of HF and H₂SO₄ acids. The solution is then treated in several chemical steps to form a colored complex for spectrophotometric measurement. There was some concern that radiolysis effects in the solution from the dissolved radionuclides could alter the measured Fe(II)/Fe(III) ratio, resulting in unreliable indications of glass melt redox conditions.

Tests indicated that the radiation dose rate from the dissolved radionuclides in DWPF glass is too low to significantly affect Fe(II)/Fe(III) ratio measurements in glass. This was shown by direct comparison of the method with Fe-57 Mossbauer spectroscopy. Since Fe-57 Mossbauer spectroscopy is a non-destructive, solid phase technique, the Fe(II)/Fe(III) ratio is not affected by radiation. Simulated defense waste glass containing 0.10 Ci/g of beta-gamma radiation from equal contributions of Sr-90 and Cs-137 was analyzed by both methods. The colorimetric technique gave a value of 0.24 ± 0.03 for the Fe(II)/Fe(III) ratio vs. 0.18 ± 0.04 obtained by Mossbauer [8]. Agreement of the methods within their observed precision limits indicates that radiation does not greatly affect the colorimetric method.

CONCLUSIONS

The results presented in this paper support the following conclusions:

1. The compositions of high-level radioactive sludges and glasses can be accurately and precisely determined using remote dissolution procedures followed by ICP-AES, AAS, and radioactive analyses.
2. For radioactive glasses, the sodium peroxide fusion and microwave-acid dissolution methods are well suited. To minimize the possibility of contamination in the hot cell environment, the microwave-acid dissolution method is favored. Based on analyses of replicate samples, the precision is 5% or better for the major radioactive and nonradioactive components. Concurrent analyses of a

standard glass indicate that the analyses are very accurate.

3. For radioactive sludges, the sodium peroxide fusion and aqua regia dissolution methods are well suited. Based on analyses of replicate samples, the precision is 5% or better for the major components. The results of both methods are in excellent agreement suggesting that the results are accurate.
4. The Fe(II)/Fe(III) ratio in radioactive glasses can be accurately determined by remote colorimetric techniques.

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REFERENCES

1. R. Maher, L. F. Shafranek, J. A. Kelley, and R. W. Zeyfanf, "Solidification of Savannah River High-Level Waste," American Nuclear Society Transactions, 39, p.228, 1981.
2. U.S. Department of Energy Office of Civilian Radioactive Waste Management, "Waste Acceptance Preliminary Specifications for the Defense Waste Processing Facility High-Level Waste Form," USDOE Report DOE/RW-0125 OGR/B-8 December (1986).
3. E. F. Sturcken, T. S. Floyd, and D. P. Manchester, "Remote Operation of Microwave System," Chapter 9 in "Introduction to Microwave Sample Preparation," H. M. Kingston and L. B. Jassie, Editors, pp. 187-202, American Chemical Society, Washington, DC, 1988.
4. E. W. Baumann, C. J. Coleman, D. G. Karraker, and W. H. Scott, USDOE Report DP-MS-87-18, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Inc., Aiken, SC (1987).
5. D. R. Van Hare and W. S. Prather, "Fiber Optic Modification of a Diode Array Spectrophotometer," USDOE Report DP-1714, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Inc., Aiken, SC (1986).
6. J. A. Stone, J. A. Kelley, and T. S. McMillan, "Sampling and Analyses of SRP High-Level Waste Sludges," USDOE Report DP-1399, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Inc., Aiken, SC (1976).

7. R. G. Baxter, "Description of the Defense Waste Processing Facility Waste Form and Canister," USDOE Report DP-1606, Rev. 2, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Inc., Aiken, SC (1988).

8. C. J. Colemann, E. W. Baumann, N. E. Bibler, R. A. Dewberry, and E. F. Sturcken, "Analysis of Radioactive Waste and Glass for a Defense Waste Solidification Plant," USDOE Report DP-MS-87-23, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Inc., Aiken, SC (1987).

TABLE 1. Analysis of a Standard Simulated Nuclear Waste Glass

<u>Oxide</u>	<u>SRS Results^a</u> (wt%)	<u>Standard Results^b</u> (wt%)
SiO ₂	46.0 ± 0.5 ^c	45.4 ± 0.11
Fe ₂ O ₃	13.6 ± 0.2 ^d	13.2 ± 0.10
Na ₂ O	11.7 ± 0.1 ^d	11.8 ± 0.04
B ₂ O ₃	9.27 ± 0.06 ^c	9.22 ± 0.08
Li ₂ O	3.06 ± 0.03 ^d	3.06 ± 0.02
Al ₂ O ₃	3.94 ± 0.10 ^d	4.10 ± 0.04
MnO ₂	3.44 ± 0.03 ^d	3.54 ± 0.02
CaO ^d	1.32 ± 0.03 ^d	1.30 ± 0.02
MgO	1.23 ± 0.02 ^d	1.21 ± 0.02
NiO	1.23 ± 0.07 ^d	1.12 ± 0.03
TiO ₂	1.02 ± 0.02 ^d	1.05 ± 0.01
U ₃ O ₈	2.28 ± 0.08 ^d	2.32 ± 0.01
K ₂ O	3.09 ± 0.03 ^e	3.00 ± 0.02
Sum	101.2	100.3

^aAverage and standard deviation of 6 samples dissolved remotely.

^bPrepared and analyzed by Corning Glass Works, Corning, NY.
Average and Standard Deviation of 5 to 10 determinations.

^cNa₂O₂ fusion dissolution method followed by ICP-AES analysis.

^dMicrowave-Acid dissolution method followed by ICP-AES analysis.

^eMicrowave-Acid dissolution method followed by AAS analysis.

TABLE 2. Major Components of Two Radioactive SRS Nuclear Waste Glasses

Nonradioactive Oxides (wt%)

<u>Oxide</u>	<u>200R</u>	<u>165/42</u>	<u>Oxide</u>	<u>200R</u>	<u>165/42</u>
B ₂ O ₃	9.46	8.24	Al ₂ O ₃	4.62	10.9
Li ₂ O	3.01	5.16	Fe ₂ O ₃	12.3	6.49
Na ₂ O	13.29	12.0	CaO	1.47	0.37
K ₂ O	3.49	0.0	MgO	1.25	1.07
SiO ₂	45.1	56.6	MnO ₂	2.61	2.05
U ₃ O ₈	0.4	0.17	NiO	0.53	0.64

Radionuclides (mCi/100 g glass)

<u>Radionuclide</u>	<u>200R</u>	<u>165/42</u>
Cs-137	1.76	9.1
Sr-90	50.7	1090.
Sb-125	0.09	0.34
Eu-154	0.23	3.8
Eu-155	0.18	8.6
Alpha ^b	1.0	4.2

^aResults of dissolutions of 10 to 18 samples. Precision for elements > 1 wt.% and for Cs-137 and Sr-90 was 6% or less. For others, ~ 10%.

^bPrimarily Cm-244 and Pu-238.

TABLE 3. Averages and Standard Deviations for the Concentrations (wt%) of Important Nonradioactive Elements in Washed, Dried SRS Tank 51 Sludge Dissolved by Two Methods.

Element	Concentration (wt%)	
	Na ₂ O ₂ Fusion ^a	Aqua-Regia ^a
Fe	30.5 ± 0.80	30.6 ± 0.46
Al	8.88 ± 0.23	8.92 ± 0.14
Na	b	4.02 ± 0.27
Mn	3.21 ± 0.15	3.30 ± 0.05
Ca	2.93 ± 0.04	2.91 ± 0.05
Mg	1.52 ± 0.03	1.53 ± 0.02
Si	0.92 ± 0.04	0.60 ± 0.04
P	0.64 ± 0.02	0.63 ± 0.02
Ni	b	0.37 ± 0.02
Cr	0.20 ± 0.01	0.21 ± 0.01
Zn	0.15 ± 0.08	0.17 ± 0.01
K	c	0.01 ± 0.004
Hg	c	0.023 ± 0.001

^aAverage and standard deviation from the dissolution of nine samples of dried sludge.

^bNot determined due to analytical interferences

^cDetermined by AAS on aqua regia dissolutions.

TABLE 4. Averages and Standard Deviations for the Concentrations (mCi/100 g) of Major Radioactive Elements in Washed, Dried SRS Tank 51 Sludge Dissolved by Two Methods

Radionuclide	Concentration	
	Na ₂ O ₂ Fusion ^a	Aqua-Regia ^a
Sr-90	96.9 ± 2.4	b
Cs-137	7.51 ± 0.20	7.56 ± 0.28
Am-241	1.41 ± 0.02	1.40 ± 0.04
Ce-144	1.24 ± 0.03	1.22 ± 0.02
Eu-154	0.33 ± 0.01	0.40 ± 0.13
Co-60	0.29 ± 0.01	0.28 ± 0.01
Eu-155	0.15 ± 0.01	0.19 ± 0.09
Total Alpha ^c	10.7 ± 0.7	11.9 ± 1.2
Total U (weight %)	3.45 ± 0.04	3.59 ± 0.09

^aAverage and standard deviation from the dissolution of nine samples of sludge.

^bResults were very imprecise presumably due to counting interferences and thus considered unreliable

^cNominally 10% Cm-244, 10% Pu-239, and 80% Pu-238 and Am-241.

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