**WSRC-TR-2001-00514**

# Characterization of Surface and Variable Depth Samples from the 3H Evaporator Feed (32H) and Drop (30H) Tanks – Re-Baseline of Silicon Concentration and Aluminosilicate Formation

W. R. Wilmarth, J. T. Mills, V. H. Dukes, and R. C. Sullivan
Westinghouse Savannah River Site
Aiken, SC 29808

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161, phone: (800) 553-6847, fax: (703) 605-6900, email: orders@ntis.fedworld.gov online ordering: http://www.ntis.gov/support/index.html

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062, phone: (865 ) 576-8401, fax: (865) 576-5728, email: reports@adonis.osti.gov

## Summary

Surface and variable depth samples from the 3H Evaporator feed tank, Tank 32H, and drop tank, Tank 30H, have been analyzed at SRTC. These analyses support continued operation of the 3H Evaporator with regards to silicon concentrations and aluminosilicate formation. Results of these analyses indicate the following.

- Measured silicon concentrations (avg. 24.4 mg/L) from samples taken in March of 2001 agreed with the initial baseline of 22.75 mg/L within one measurement standard deviation. Thus, the historical maximum silicon concentration for the 3H Evaporator remains unchanged.
- The predicted sodium aluminosilicate formation for the March 2001 samples using the Gasteiger model was 0.12 g per liter of supernate evaporated three-fold. This amount of solids formation is slightly less than the historical maximum of 0.131 g.
- Mercury concentrations in supernate any of the 3H Evaporator tanks (32H or 30H) were minimal (< 75 mg/L).

**Keywords: Evaporators, Silicon Analysis, Aluminosilicate**

## Introduction

The Replacement High Level Waste Evaporator (242-25H or 3H) began radioactive operation in 2000. The 3H

Evaporator is significantly larger than the older evaporators at the Savannah River Site (SRS) and operates at higher temperatures (160°C compared to 120°C). Wilmarth, et al,[1] performed initial chemical and radiological characterization of the 3H system. The results of these studies showed the system contained a highly caustic supernate typical of historical canyon waste. These tests also showed the supernates from Tank 32H and 30H contained low concentrations of silicon. The low silicon content is important to ensure evaporator operation does not lead to aluminosilicate formation as observed in the 242-16H (2H) Evaporator.[2,3]

Additional studies[4,5] of the 3H Evaporator chemistry reaffirmed the low concentrations of silicon. As committed to in the Nuclear Criticality Safety Evaluation,[6] this report documents the results of sample analysis for samples taken in March of 2001. Additionally, samples were analyzed for mercury to assist in understanding high mercury levels in the 3H Evaporator overheads.

## Experimental Methods

SRTC received the surface and variable depth (VDS) samples from the tank farms on March 28, 2001. The surface and VDS samples from the tanks entered A-block of the Shielded Cells upon receipt at SRTC. Personnel determined the density of the liquid samples by emptying the contents of the dip bottles into pre-weighed 100-mL graduated cylinders with the accuracy of the graduated cylinders verified to ± 1% at 100 mL prior to use. Personnel removed representative aliquots and diluted one-fifty fold into 0.2 M nitric acid for radiochemical and elemental analysis and into water for anion analysis. The samples were put through a filtering protocol to determine the total amount of silicon in a given volume of liquid waste. The protocol[7] included sampling as-received waste, sequential filtration through at least 0.2 micron and 0.02 micron filters, and analyzing filtrates and filters for aluminum and silicon.

Add something on sludge filtering with 0.45 micron.Difficulty was experienced in filtering the samples containing sludge and or saltcake. The solids would effectively blind the filter. The increased residence time that the filter was in contact with the highly caustic solution caused the filter media to dissolve. This allowed sludge to breakthrough the filter and cause analysis difficulties.

Personnel placed the diluted samples in a sample bottle and removed from the shielded cell without filtering. Analytical Development Section performed the following analyses: Ion Chromatography,[8] Inductively Coupled Plasma – Mass Spectrometry,[9] Inductively Coupled Plasma – Emission Spectroscopy,[10] Gamma Spectroscopy,[11] and Alpha Pulse Height Analysis.[12]

Laboratory notebook WSRC-NB-2001-00065 contains details and results of the sample preparation procedures.[13] Personnel used routine analytical protocol for the samples in this report.[14]

## Results and Discussion

### Sample Description

Six samples were received at SRTC for re-baselining the silicon concentration and the amount of aluminosilicate solid formation. These samples were variable depth samples pulled on March 27, 2001. Most of the samples contained sludge and/or saltcake and proved difficult to filter. This difficulty did not allow the measurement of silicon in the sludge solids. The silicon values reported are for the filtrate only. An additional sample was received in June for mercury analysis.

### Sample Density and Observations

Table 1 contains the measured density of the samples as received at SRTC. The elevation listed in Table 1 for each sample reflects the height as measured from the tank bottom (tank bottom is 0 inches). The sludge height at the time of sampling was estimated to be ~ 34 inches in Tank 32H and the salt layer was at 5.3" in Tank 30H.

The measured densities ranged from 1.39 g/mL to 1.50 g/mL for the supernate samples. At an elevation near the salt layer, the density is much higher and are 1.94 g/mL. One sample (HTK-419) taken at an elevation of 5.3" exhibited a very low density (1.50 g/mL) compared to another sample (HTK-418) taken at a slightly higher elevation. This sample's deviation is not understood.

Table 1. Sample Information for 3H Evaporator System

| Sample | Tank | Elevation[15] | Density (g/mL) |
|---|---|---|---|
| HTK-412 | 32H | 34" | 1.43 |
| HTK-414 | 32H | 132" | 1.43 |
| HTK-416 | 30H | 329" | 1.39 |
| HTK-417 | 30H | 170" | 1.40 |
| HTK-418 | 30H | 11" | 1.94 |
| HTK-419 | 30H | 5.3" | 1.50 |
| HTF-440 | 32H | Surface | 1.40 |

Elevation is from tank bottom.

**Elemental Analysis**

Table 2 contains the elemental analysis of the variable depth samples from the 3H Evaporator system. Sodium ion concentrations in the supernates range from 10.1 to 13.8 M with the exception of sample HTK-418. The sodium ion concentration in this salt-laden sample measured 21 M. The value must include some insoluble sodium. Aluminum concentrations ranged from 0.83 to 1.63 M. Again the measured aluminum was very high for the sample HTK-418. The chromium concentrations ranged from near predicted average concentration (238 mg/L) to 582 mg/L. Mercury concentrations were measured in the HTK-414 through 419 along with the HTF-440 samples. Mercury concentrations in the bulk supernate phase (HTK-414 through HTK-417) were typical levels and ranged 44 mg/L to 66 mg/L. These samples could contain particulate matter that include mercury. The mercury concentration measured in the dip sample (HTF-440) was low and measured 15 mg/L.

Table 3 displays the anion concentrations measured in the 3H Evaporator samples. The hydroxide ion concentrations were high and ranged from 4.5 M to 7.8 M and averaged 5.4 M excluding sample HTK-418 for previously specified reasons. The anion – cation balance based on analytical measurements showed agreement. However, sodium ion concentrations is always higher than the anion sum.

**Table 2. Elemental Analysis of Tank 32H and 30H Samples**

| Analyte | Units | Tk 32H HTK-412 | Tk 32H HTK-414 | Tk 30H HTK-416 | Tk 30H HTK-417 | Tk 30H HTK-418 | Tk 30H HTK-419 |
|---|---|---|---|---|---|---|---|
| Al | M | 1.15 | 1.17 | 0.83 | 0.89 | 1.63 | 0.88 |
| B | mg/L | 193.21 | 195.00 | 135.44 | 137.64 | 311.80 | 206.63 |
| Ba | mg/L | 0.55 | 0.54 | < 0.15 | 0.51 | 9.32 | 5.70 |
| Ca | mg/L | < 0.05 | < 0.05 | < 0.05 | < 0.05 | < 0.37 | 9.75 |
| Cd | mg/L | 1.15 | 0.92 | 0.80 | 0.96 | 2.25 | 0.72 |
| Co | mg/L | 0.75 | < 0.15 | 0.20 | 0.61 | 2.51 | 0.21 |
| Cr | mg/L | 376.67 | 356.48 | 280.03 | 288.48 | 582.30 | 238.08 |
| Cu | mg/L | 6.25 | 6.47 | 3.97 | 4.35 | 6.07 | 6.41 |
| Fe | mg/L | 43.34 | 43.14 | 22.90 | 34.67 | 278.22 | 73.48 |
| La | mg/L | 0.65 | < 0.49 | < 0.50 | 0.56 | < 3.74 | 5.34 |
| Li | mg/L | 0.30 | < 0.15 | < 0.15 | 0.25 | < 1.12 | 0.41 |
| Mg | mg/L | 0.85 | 0.92 | 0.75 | 0.91 | 17.63 | 5.54 |
| Mn | mg/L | 1.60 | 1.56 | 0.85 | 1.01 | 234.82 | 88.46 |
| Mo | mg/L | 271.75 | 262.22 | 186.42 | 191.65 | 462.23 | 148.13 |
| Na | M | 11.2 | 11.5 | 10.1 | 10.1 | 21.0 | 13.8 |
| Ni | mg/L | 0.90 | < 0.44 | < 0.45 | 8.10 | 67.84 | 20.01 |
| P | mg/L | 332.43 | 363.97 | 273.90 | 278.87 | 648.27 | 206.88 |
| Pb | mg/L | 38.09 | 33.90 | 24.81 | 26.58 | 60.50 | 24.37 |
| Si | mg/L | 22.05 | 18.58 | 16.87 | 18.48 | 96.93 | 39.25 |
| Sn | mg/L | 35.04 | 33.46 | 22.35 | 23.79 | 81.51 | 23.29 |
| Sr | mg/L | 0.15 | 0.10 | 0.10 | 0.15 | 2.55 | 1.90 |
| Ti | mg/L | 0.20 | < 0.05 | < 0.05 | 0.25 | 2.10 | 0.10 |
| U | mg/L | 14.65 | 5.74 | < 3.87 | 14.17 | 70.65 | 18.06 |
| V | mg/L | 3.95 | 3.45 | 2.81 | 3.09 | 7.97 | 1.39 |
| Zn | mg/L | 10.65 | 10.51 | 10.14 | 12.55 | 11.01 | 18.37 |
| Zr | mg/L | 1.90 | 1.41 | 0.25 | 0.76 | 24.19 | 3.95 |
| Hg | mg/L | | 66.30 | 44.36 | 53.30 | | |

**Table 3. Anion Concentrations in Tank 43H**

| Analyte | Units | Tk 32H HTK-412 | Tk 32H HTK-414 | Tk 30H HTK-416 | Tk 30H HTK-417 | Tk 30H HTK-418 | Tk 30H HTK-419 |
|---|---|---|---|---|---|---|---|
| OH | M | 5.8 | 4.6 | 4.5 | 5.3 | 7.8 | 6.8 |
| AlO2 | M | 1.2 | 1.2 | 0.8 | 0.9 | 1.6 | 0.9 |
| F | M | | < 0.020 | < 0.021 | < 0.022 | < 0.011 | < 0.02 |
| Cl | M | | < 0.020 | < 0.021 | < 0.022 | 0.017 | < 0.02 |
| NO3 | M | 1.84 | 1.60 | 1.79 | 1.65 | 2.22 | 1.75 |
| NO2 | M | 1.97 | 1.73 | 1.39 | 1.70 | 1.66 | 2.28 |
| SO4 | M | | 0.009 | 0.014 | 0.017 | 0.426 | 0.218 |
| Anion Sum | M | 10.7 | 9.1 | 8.6 | 9.6 | 13.8 | 12.0 |
| Na | M | 11.2 | 11.5 | 10.1 | 10.1 | 21.0 | 13.8 |

## Radiochemical Analysis

Table 4 contains measured concentrations of a number of radionuclides. $^{137}$Cs concentrations ranged from 5.4 x $10^9$ dpm/mL to 1.2 x $10^{10}$ dpm/mL across the tanks. These values agree with previously published results for the 3H Evaporator system.[4] We, also, measured plutonium concentrations in the samples. The combined $^{239}$Pu and $^{240}$Pu measurement in the samples showed concentrations between 3.6 x $10^4$ and 6 x $10^5$ dpm/mL. Likewise $^{238}$Pu concentration for the three samples measured from approximately 1.8 x $10^5$ to 2.9 x $10^7$ dpm/mL.

Personnel measured uranium concentrations in the tank samples and results are shown in Table 4. The total uranium concentration varied widely from 3.1 mg/L to 14.1 mg/L. The $^{235}$U enrichment measurements showed averaged 15.1 % across the 3H evaporator system.

**Table 4. Radionuclide Results from 3H Evaporator Samples**

| Analyte | Units | Tk 32H HTK-412 | Tk 32H HTK-414 | Tk 30H HTK-416 | Tk 30H HTK-417 | Tk 30H HTK-418 | Tk 30H HTK-419 |
|---|---|---|---|---|---|---|---|
| Cs-137 | dpm/mL | 7.45E+09 | 7.44E+09 | 5.37E+09 | 5.52E+09 | 1.16E+10 | 8.00E+09 |
| Pu-239/240 | dpm/mL | 5.35E+04 | 3.56E+04 | 3.82E+04 | 4.28E+04 | 5.88E+05 | 6.05E+05 |
| Pu-238 | dpm/mL | 6.80E+05 | 1.81E+05 | 1.10E+06 | 1.07E+06 | 2.89E+07 | 1.46E+07 |
| 234 | ppb | | | 2.84E+02 | | | 2.37E+02 |
| 235 | ppb | | 7.11E+02 | 2.24E+03 | 4.81E+02 | 4.02E+02 | 1.95E+03 |
| 236 | ppb | | 3.57E+02 | 1.06E+03 | 2.24E+02 | | 9.25E+02 |
| 237 | ppb | | | | | | |
| 238 | ppb | | 3.05E+03 | 1.05E+04 | 2.40E+03 | 3.29E+03 | 8.95E+03 |
| 239 | ppb | | | 3.78E+02 | 0.00E+00 | 0.00E+00 | 1.73E+02 |

The formation of sodium aluminosilicate solids during 2H evaporator operation has proved very detrimental.[16] Pursuant to that, commitments were established to operate in a manner that would minimize aluminosilicate solids formation, which included periodic sampling and measurement of silicon and aluminum concentrations in waste solutions fed to the evaporator systems. A protocol was developed to ascertain the total silicon concentration to include dissolved and colloidal species. Table 5 contains the silicon concentrations measured in the 3H Evaporator samples. As previously mentioned, we were unable to secure the filters for analysis. There is some evidence that colloidal silicon exists because the as-received silicon measurement on sample HTK-418 measured 97 mg/L. However, the filtered supernates from all of the samples measured much lower. Previous studies indicated the amount of colloidal silicon is very low.[4] Therefore, the total silicon concentrations may be slightly higher than presented in Table 5.

The highest measured silicon concentration was for the sample HTK-418. However as previously mentioned, this sample contained salt. The samples from the supernate phase (HTK-412 through HTK-417 and HTK-419) averaged 24.4 mg/L with a standard deviation of 4.2. This average silicon concentration is slightly higher than the previously derived maximum historical concentration[17] of 22.75 mg/L. However, the new average is within one standard deviation of the baseline silicon concentration has risen slightly. Therefore, the historical maximum silicon concentration remains unchanged.

The second factor of importance is the amount of sodium aluminosilicate solids that are produced during an evaporation step. Typically, we have modeled using an equation provided by Gasteiger that has previously been described.[1] In this model, we estimate the difference in total silicon concentration and soluble silicon concentration. We correct the silicon concentration to sodium aluminosilicate mass for a given concentration factor in the evaporator, normally 3. For the 3H Evaporator, the amount of solids formation[17] was established at a level of 0.131g of aluminosilicate per liter of supernate that was evaporated three-fold.

**Table 5. Total Silicon (mg/L) in 3H Evaporator Samples**

| Sample | Tank | Silicon Conc. |
|---|---|---|
| HTK-412 | 32H | 23.2 |
| HTK-414 | 32H | 20.7 |
| HTK-416 | 30H | 24.5 |
| HTK-417 | 30H | 22.2 |
| HTK-418 | 30H | 34.8 |
| HTK-419 | 30H | 31.4 |

Using the measured average silicon concentration of 24.4 mg/L and the averaged sodium and aluminum ion concentrations from Table 2 and the averaged hydroxide concentrations from Table 3 for the samples HTK412 through

HTK-417, we estimated a solids formation of 0.12 g of aluminosilicate per liter of supernate. This solids formation rate is below the aforementioned maximum historical value of 0.131 g. The current formation rate is lower due to the higher ionic strength and steady silicon concentration. The pseudo equilibrium solubility product, $K_{sp}$, for the silicon and aluminum concentrations has a measured value of $8 \times 10^{-4}$ $M^2$. This value is slightly higher than the baseline value of $6.5 \times 10^{-4}$ $M^2$.

## Conclusions

The Replacement High Level Waste Evaporator (242-25H or 3H) began radioactive operation in 2000. As part of the evaporator's authorization basis, surface and variable depth samples from the feed tank, Tank 32H, and drop, Tank 30H, tanks from the 3H Evaporator are to be routinely analyzed with regards to silicon concentrations and aluminosilicate formation.

Measured silicon concentrations (avg. 24.4 mg/L) from samples taken in March of 2001 agreed with the initial baseline of 22.75 mg/L within one standard deviation. Thus, the historical maximum silicon concentration for the 3H Evaporator remains unchanged. The predicted sodium aluminosilicate formation for the March, 2001 samples using the Gasteiger model was 0.12 g per liter of supernate evaporated three-fold. This amount of solids formation is slightly less than the historical maximum of 0.131 g. Lastly, mercury concentrations in supernate were measured due to operational difficulties with the mercury concentrations in the evaporator overheads. The measured mercury concentration in the 3H Evaporator tanks (32H or 30H) was minimal (< 75 mg/L).

## Acknowledgments

The authors greatly appreciate the hard work and dedicated support of the Analystical Development staff. In particular, the support of June Hart, Lorreta Farrow, Ci Ci and Dave Diprete, Pam Waller, Bill Boyce and Mira Malek.

## References

1. W. R. Wilmarth and R. A. Peterson, "Analyses of Surface and Variable Depth Samples from Tanks 30H and 32H," WSRC-TR-2000-00112, April 3, 2000.
2. W. R. Wilmarth, C. J. Coleman, A. R. Jurgensen, W. M. Smith, J. C. Hart, W. T. Boyce, D. Missmer, and C. M. Conley, "Characterization and Dissolution Studies of Samples from the 242-16H Evaporator," WSRC-TR-2000-00038, Rev. 0, January 31, 2000.
3. W. R. Wilmarth, C. J. Coleman, J. C. Hart, and W. T. Boyce, "Characterization of Samples from the 242-16H Evaporator Wall," WSRC-TR-2000-00089, March 20, 2000.
4. W. R. Wilmarth, V. H. Dukes, J. T. Mills, C. J. Coleman, J. C. Hart, W. T. Boyce, and R. L. Cadle, "Characterization of Samples from the 3H Evaporator System including Effects of Recycle," WSRC-TR-2000-00399, October 15, 2000.
5. W. R. Wilmarth, "Technical Requirements for Dispositioning Tank 40H Decants," SRT-LWP-2001-00032, March 3, 2001.
6. R. Ross, "Nuclear Criticality Safety Assessment of the 242-25H Evaporator (U)," WSRC-TR-2000-00069, Rev. 0, March 2, 2000
7. W. R. Wilmarth, V. H. Dukes, J. T. Mills, C. J. Coleman, J. C. Hart, W. T. Boyce, C. C. Diprete, and R. L. Cadle, "Characterization of Tank 40H Supernate and Hydroxide Washing of Sludge," WSRC-TR-2000-00353, September 15, 2000.
8. "Analysis of Solutions by Ion Chromatography," Manual L16.1, Procedure ADS 1543, Rev. 1, April 1, 1998.
9. "Inductively Coupled Plasma - Mass Spectrometer Elemental and Isotopic Analysis for Aqueous Liquid Sample Fisons PlasmaQuad II (U)," Manual L16.1, Procedure ADS1543, Rev. 1, April 1, 1998.
10. "Inductive Coupled Plasma - Emission Spectrometer for Aqueous Liquid Sample Analysis," Manual L16.1, Procedure ADS-1509, June 25, 1996.
11. "Gamma Sample Preparation and Analysis (Gamma PHA)," Manual L16.1, Procedure ADS-2420, Rev. 3, July 28, 1997.
12. "Alpha Pulse Height Analysis," Manual L16.1, Procedure ADS-2402, Rev. 2, July 25, 1994.

13. "Technical Notebook Use," Savannah River Technology Center Procedures Manual, L1, Procedure 4.19, Rev. 5, February 2, 1998.
14. "Obtaining Analytical Services," Savannah River Technology Center Procedures Manual, L1, Procedure 3.07, Rev. 0, August 6, 1993.
15. J. Gillam, "43H Samples," electronic mail message, January 22, 2001.
16. C. S. Boley, M. C. Thompson, W. R. Wilmarth, K. G. Brown, "Technical Basis for the 242-16H Evaporator Cleaning Process (U)," WSRC-TR-2000-00211, Rev. 1, November 7, 2000.
17. W. R. Wimarth, "Tank 40H Sample Analysis results 4th Set Second Decant and Effect of 3H Evaporator System," SRT-LWP-2001-00039, April 6, 2001.