WSRC-MS-2001-00237

Evaporation of a Large Decontaminated Hanford Tank Sample

C.L. Crawford, M. L. Crowder, H.H. Saito, and T.B. Calloway
Westinghouse Savannah River Company
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/ordering.htm

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

Introduction

A radioactive sample (~15 L) from Hanford tank 241-AN-102 was concentrated via evaporation at reduced pressure and temperature, to support flowsheet development and regulatory approval for the Hanford River Protection Project Waste Treatment Plant (RPP-WTP). The received sample (Envelope C) had been pretreated at the Savannah River Technology Center (SRTC) for removal of strontium and transuranic ions by precipitation and removal of cesium and technetium via ion exchange. The resulting pretreated Low Activity Waste (LAW) stream was the feed material for this evaporation test. The goals of this evaporation were to: (1) provide operating data -- including foaming and scaling tendencies -- for scale-up purposes, (2) obtain liquid and off-gas samples during steady-state operation for regulatory analysis, (3) conduct a "final boildown" after the steady-state operation to determine the solubility endpoint of the solution and the major precipitants, and (4) provide concentrated feed for a melter vitrification study to produce several kilograms of immobilized LAW glass product.

Experimental

Figure 1 shows a diagram of the bench-scale evaporator unit. Dose rates from the pretreated sample allowed contact handling of the experiment in a radiochemical hood. The evaporator pot was designed based upon a natural-circulation calandria (thermosiphon reboiler). Thermo-siphon evaporators operate by density differences between the liquid entering the heat exchanger and the two-phase vapor-liquid mixture that is generated in and exits the heat exchanger. This design was also used in an earlier simulant study at SRTC [Saito et al., 2001]. The liquid in the evaporator is mixed with a magnetic stirrer. To increase flow to the heater, the liquid lines between the evaporator and the heater are mounted tangentially to the mixing of the solution inside the evaporator.

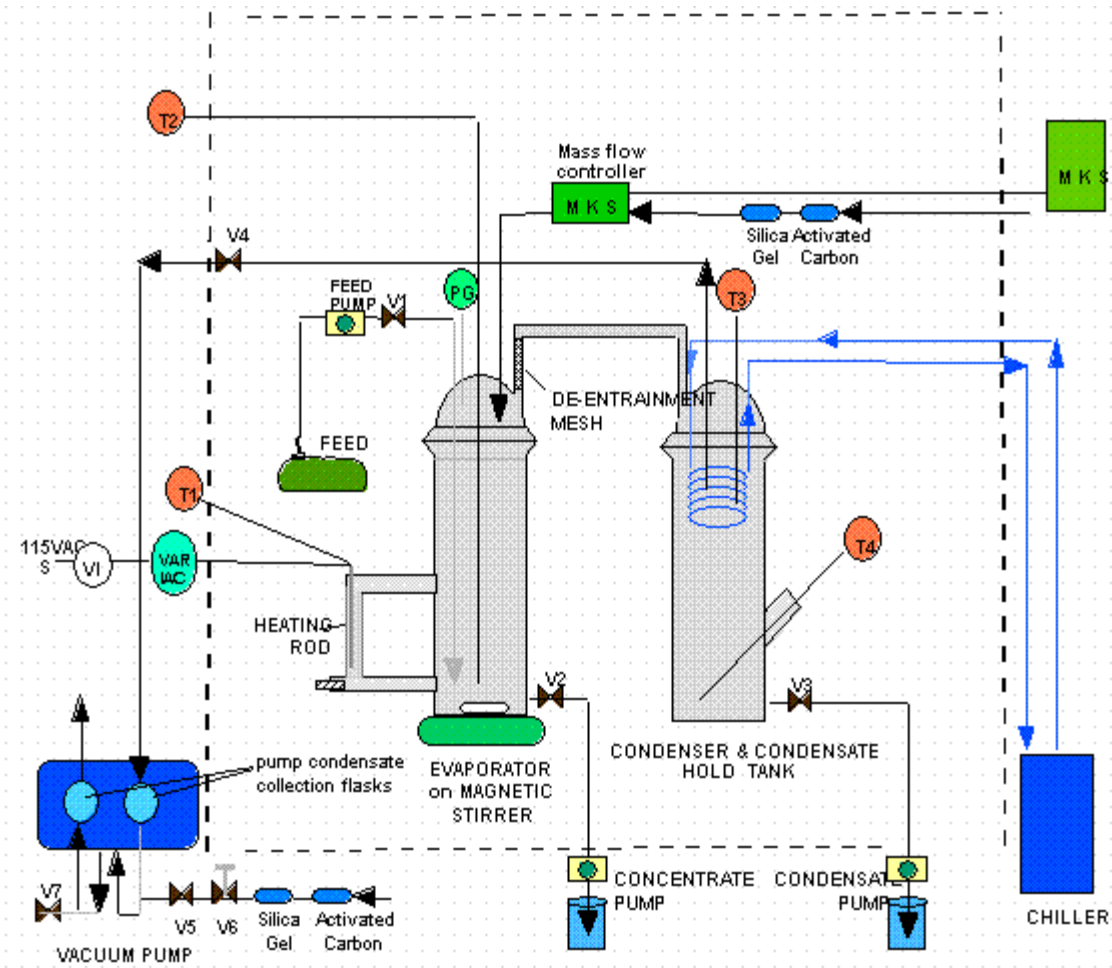

Figure 1. Bench Scale Evaporator

The evaporator was heated using a corrosion and oxidation resistant IncoloyÒ 1000 W resistance heater. The heater had an internal thermocouple that gave a reasonable approximation of the heater surface temperature. The primary indication of scaling was visual. The bench-scale evaporator was initially charged with approximately 1.5 L of Envelope C feed with a specific gravity of 1.23 g/ml. The system pressure was maintained at 9.46 ± 1 kPa (71 ± 8 torr). This pressure was calculated by the SRTC LAW Evaporator OLI Environmental Simulation Program (ESP) model, and represented the steady-state operating pressure required at 50° C to reach the desired evaporation endpoint. The condenser temperature was maintained at 40 ± 3° C which is the design basis temperature for the RPP-WPT pretreated LAW evaporator. The heat flux through the heater rod was maintained at 6.0 to 6.3 W/cm^2 during the steady-state portions of the experiment. This heat flux represents about 75% of the design basis for the RPP LAW Melter Feed Evaporator (8.13 W/cm^2). System vacuum was maintained using an oil-free PTFE diaphragm vacuum pump that was capable of an ultimate vacuum of 9 torr. The vacuum pump was connected to the system with 304-L stainless steel tubing and TeflonÒ tubing. To minimize entrainment, the overhead tube between the evaporator and condenser was packed with 6" of stainless steel mesh and had a "J"-shaped inlet port. The evaporation experiment consisted of an initial boildown in which the initial batch of salt solution (4.9M sodium) was allowed to concentrate to a predetermined endpoint, selected by the RPP customer as 80% of the bulk solubility at 25° C, or a target of ~ 7.1M sodium. Once the endpoint concentration was reached during the initial boildown, the steady-state portion of the experiment was started. During steady-state evaporation, the evaporator feed pump and discharge pumps were started, and their flow rates were set based on the measured condensate rate and desired concentrate concentration at a range of 2 to 6 mL/min. The unit was operated under steady-state conditions for three ten-hour segments, each corresponding to a different offgas sampling method: volatiles (Method 0031), metals/radionuclides (Method 0060), and semivolatiles (Method 0010), sampled in that order. The Method numbers refer to different SW-846 protocols established by the Environmental Protection Agency (EPA), and are termed regulatory analyses. The evaporator was shut down between these ten-hour segments to facilitate sampling, change of offgas sampling equipment, and drainage

of the condenser. Concentrate samples were taken periodically during the volatiles offgas sampling portion of the experiment and submitted for regulatory and in-house analysis. Two 1-L samples of concentrate from the semivolatiles portion of the experiment were submitted for multiple regulatory analyses. The remaining concentrate from different portions of the experiment was combined to provide feed for the LAW Melter for vitrification.

A list of typical values for steady-state evaporator operation is provided below.

VI volts	VI amps	T1 ºC	T2 ºC	PG in. Hg	T3 ºC	T4 ºC	Air in-leakage mL/min
41	3.32	67.2	51.1	-26.9	40.2	33.6	11.5

Results and Discussion

Initial Boildown: The radioactive liquid was concentrated from ~5 M to ~7.1 M sodium (Na). Significant foaming was observed. Therefore, antifoam was added periodically to prevent foaming over the evaporator. Specifically, the antifoam (Dow US 1520) was added @ 1 g/L every 2-3 hours. Alternatives will be investigated to reduce the amount of antifoam required.

Steady State Evaporation: During steady-state operation, offgas samples were obtained for three different EPA SW-846 offgas methods. The offgas stream passed through either resin beds or liquid solutions, depending on the prescribed method. The resulting offgas samples, along with many liquid samples of concentrate, condensate, and their associated process blanks, field blanks, and trip blanks, were shipped offsite to an EPA-approved laboratory and analyzed. In addition, SRTC analyzed some concentrate and condensate liquid samples for inorganic, radionculide and limited volatile and semi-volatile organic characterization. The decontamination factor, DF, is defined as the ratio of the concentration in the feed to that in the condensate. For major components in the feed, Al, Cr, Na, P, and Sr, the DF across the evaporator was approximately 10^4 - 10^5. The gamma-emitting isotopes, all had DF values greater than 10^4. Taken together, DF values indicate that entrainment was effectively minimized by the demister in the overhead tube between the evaporator and the condenser. The concentration factor, CF, is the ratio of the concentration in the concentrate to that in the feed. Based on total volume, the expected CF is 1.53. For this study, the average CF for most of the elements was 1.54 with an error range of ±10%.

Organic Analysis: Tetrahydrofuran (THF) was the only volatile organic compound (VOC) detected, and was present in both concentrate and condensate at ~200 ppb. Other VOC's from a list of 38 EPA-regulated compounds were not detected above the instrument detection limits ranging from 1 to 5 mg/L. Twelve semivolatile organic compounds (SVOC) were detected in the concentrate (at 1 to 20 ppm), and two of these were also found in the condensate (< 1 ppm). Three of the SVOCs were alcohols that did not contain other functional groups. A diamine was detected, as was tributyl phosphate, a common extractant in actinide operations. Four SVOCs could not be identified, and three could only be assigned to a general group. Organic analyses of the evaporator feed and the products including offgas analyses according to SW-846 protocol were conducted and will be reported in the future.

Final Boildown: After the steady-state experiment and regulatory sampling were complete, a final boildown of the Envelope C solution was conducted to determine the solubility endpoint. Comparison of the wt% insoluble solids in the range of 0.94 to 1.90 wt% insoluble solids, to the starting concentrate value of 0.29 wt% insoluble solids indicates that the amount of insoluble solids increased with final boildown concentration of the concentrate. The final sample of the final boildown demonstrated a dramatic solubility endpoint, in which measured insoluble solids increased eight-fold in a few minutes to 15.9 wt%. These solids were submitted for x-ray diffraction (XRD), which showed sodium carbonate hydrate, $Na_2CO_3 \cdot H_2O$, as the major precipitant at the endpoint. XRD also identified sodium oxalate, $Na_2C_2O_4$, in all samples, as predicted by the OLI ESP model.

Conclusions

Significant foaming occurred in the Melter Feed Evaporator for pretreated Envelope C (AN102). Dow 1520-US antifoam eliminates foaming in pretreated Envelope C liquid, but additions of 1 g/L were necessary every two to three hours. Loss of effectiveness is attributed to both dilution effects and likely chemical breakdown at high pH. Scaling was not observed on the heater during steady-state operation, which involved heat flux values of 6.0 to 6.3 W/cm^2. The experimental evaporator effectively concentrated the feed solution, as gamma-producing radionuclides were all below detection limits (typically 1×10^{-6} mCi/mL) in the condensate. Only the volatile component THF was detected in the final concentrate and condensate samples – other EPA-regulated VOCs were not detected above ppb levels. Semivolatile compounds were mainly detected in the concentrate product. Consistent with OLI ESP model predictions, sodium oxalate solids (at 0.3 wt% insoluble solids) were present in the evaporator at steady-state conditions (7.1 M Na). During the final boildown, a dramatic solubility endpoint occurred at ~8.2 M Na. The dominant precipitating species was $NaCO_3 \cdot H_2O$, likely due to uptake of CO_2 from the atmosphere to yield this compound. The OLI ESP model had predicted the double salt, $Na_7F(PO_4)_3 \cdot 19H_2O$ as the major precipitant, with saturation at 8.5 M Na, but it was only found in small quantities.

Reference

1. Saito, H. H., et.al., Regulatory Off-Gas Analysis from the Evaporation of Hanford Simulated Waste Spiked with Organic Compounds, WSRC-MS-2001-00235, Westinghouse Savannah River Company, Aiken, SC